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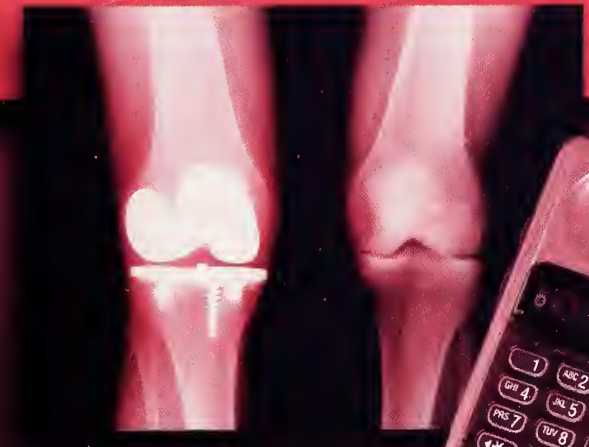
PUBLICATIONS

CERAMICS

1999 PROGRAMS AND ACCOMPLISHMENTS



MATERIALS SCIENCE AND ENGINEERING LABORATORY

NISTIR 6433

UNITED STATES DEPARTMENT OF COMMERCE

TECHNOLOGY ADMINISTRATION

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New Materials for New Applications

Advanced ceramics are vital to many products which enhance our lives. These materials provide the functional properties that enable compact wireless communication, efficient aircraft engines and durable medical replacement joints. The Ceramics Division continues a research program which develops measurement methods and standards based on scientific research to support commerce in these materials and the devices in which they are used.

UNITED STATES DEPARTMENT OF COMMERCE
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MATERIALS SCIENCE AND ENGINEERING LABORATORY

CERAMICS

1999 PROGRAMS AND ACCOMPLISHMENTS

Stephen W. Freiman, Chief

Stanley J. Dapkunas, Deputy

NISTIR 6433

January 2000

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EXECUTIVE SUMMARY

The mission of the Ceramics Division is:

Work with industry, standards bodies, academia, and other government agencies in providing the leadership for the Nation's measurements and standards infrastructure for ceramic materials.

The range of ceramic materials on which we work is broad, ranging from oxides and nitrides to materials resembling semiconductors, pertinent to a wide spectrum of important applications. Throughout this range of materials, there are common measurement issues, e.g., phase content, role of microstructure on properties, and brittle material design.

The activities of the Division are organized in the form of Programs, emphasizing a desire to foster collaborations within the Division as well as throughout the Materials Science and Engineering Laboratory, and to conduct focused activities on a scale that can lead to greater benefits for the U.S. ceramics community. The Programs are made up of projects whose primary goal is the development of measurement techniques and standards. Activities such as the development of Standard Reference Materials and databases are integrated within the relevant Programs.

Electronic and optoelectronic applications are the fastest growing market for ceramics. These materials are frequently used in film form, and our Ceramic Thin Film Program is addressing generic measurement issues associated with a broad range of applications for film devices. During the past year we established a panel representing electronic and optoelectronic industries to advise the Film Program as to the measurement and standards needs of these communities. We have also expanded activities related to materials for wireless communication, and continue to examine the needs of this particular industry sector.

We continue to look for improved ways to develop meaningful communication with our customers, i.e. the engineers and scientists in both companies and universities who use the measurement tools that we are developing. Workshops continue to be an important way for us to identify industrial measurement needs. During this past year we held a workshop addressing coating metrology issues that has led to a reformulation of our Ceramic Coatings Program. Another technique for improved communication which we have found is through consortia where direct commentary and feedback from the members occurs frequently. We currently have two active consortia: Ceramic Machining and Wear of Biomaterials.

During the past year, the Powder Processing and Ceramic Machining Programs were combined into a unified program entitled Ceramic Manufacturing. This program is now being led by Said Jahanmir. As part of this program restructuring, we also changed the goals and objectives of the CPCC, now called the Ceramic Processing Characterization Council. The CPCC is helping us to set priorities for measurement development related to ceramic manufacturing.

Last year, we created the "Ceramic WebBook," our concept of how to deliver important data on ceramic materials. During FY99 we continued to expand our efforts in the arena of informatics; the technology of data collection, formatting, and dissemination. As a means of enhancing data transfer from one database to another, we have begun an effort in the development of a transfer language (MatML) specifically designed for materials data. In addition, the Crystallographic Data Center was transferred to the Ceramics Division to facilitate linking this database with that on phase equilibria. Our long term goal is to link these two databases with the x-ray diffraction database held by the International Center for Diffraction Data.

The new synchrotron beamline at the Advanced Photon Source in Argonne, Illinois is now operational. The APS is the premier synchrotron radiation source in the world, and will provide a unique venue for the development of the next generation of measurements for materials with increasingly smaller features.

Stephen W. Freiman
Chief, Ceramics Division

CERAMIC COATINGS

The Ceramic Coatings Program addresses the development of measurement and characterization methods which will improve processing reproducibility and performance prediction of ceramic coatings. The program addresses plasma spray deposited and physical vapor deposited ceramic thermal barrier coatings (TBCs) used in aircraft and land-based turbines and diesel engines and wear resistant coatings used in many applications. These materials are a significant portion of the nearly one billion dollar North American ceramic coatings market. Collaborations have been established with industrial organizations to enable research on relevent materials and to transfer results to users. Collaborators include Pratt and Whitney, General Electric, Caterpillar, METCO, Praxair Coating Technologies, as well as the Thermal Spray Laboratory at the State University of New York at Stony Brook, NASA Lewis Research Center and the Thermal Spray Laboratory at Sandia National Laboratory. The program includes collaboration with the National Mechanical Engineering Laboratory, in Japan, to examine functionally gradient materials. Collaborations are also underway with Bundesanstalt fur Materialfurschung und -prufung) (BAM) and Deutsche Forschungsanstalt für Luft-und Raumfahrt (DLR) , both in Germany, for the development of characterization techniques for thin, hard coatings and TBCs.

Participants in the NIST program are located in the Ceramics Division, Materials Reliability Division, Metallurgy Division and NIST Center for Neutron Research of the Materials Science and Engineering Laboratory and the Chemical Science and Technology Laboratory.

The approach taken in the research has been to build on the analytical capabilities at NIST and the material processing capabilities of collaborators. The program has the following elements:

- development of techniques for characterization of physical and chemical properties of stabilized zirconia and tungsten carbide feedstock to provide data for increased processing reproducibility as well as data required for production of a Standard Reference Material suitable for calibration of light-scattering size distribution instruments used in industry for analysis of plasma-spray (PS) powder;

- development of neutron scattering techniques to determine the quantity, size and orientation of porosity and microcracks in PS ceramic coatings suitable for use in modeling the thermomechanical behavior of these materials;

- development of methods to measure chemical, elastic modulus, and thermal properties on a scale suitable for use in microstructural models of behavior;

- development of techniques to model thermomechanical behavior of thermal barrier coatings to enable more reliable performance prediction;

- development of techniques for accurate measurement of the thermal conductivity of PS and physical vapor deposition (PVD) coatings, by use of the guarded hot plate technique suitable for incorporation in ASTM standards and by the pulsed laser heating technique, to provide a method for comparison with routine industrial techniques; and

- development and refinement of more sensitive methods for accurate analysis of oxide phases and residual stresses which affect performance and durability of coatings.

Research on chemical mapping of powders and microstructures is conducted in the Microanalysis Division of the Chemical Science and Technology Laboratory. Thermal property research is conducted in the Materials Reliability and Metallurgy Divisions. The NIST Center for Neutron Research participates in phase analysis and residual stress measurement projects. A strong attribute of the coatings research program is the use of common materials for which complementary data can provide a more complete understanding of processing-microstructure-property relationships.

PROGRAM TITLE: Ceramic Coatings

PROJECT TITLE: Characterization of Thermal Spray Zirconia Powders

Principal Investigators: Stanley J. Dapkunas, Patrick Pei, James F. Kelly, Judith Stalik (NIST Center for Neutron Research) and Eric Steel (Chemical Science and Technology Laboratory)

Technical Objective:

The objective of this research is to develop measurement methods for those characteristics of thermal spray feedstock which determine the microstructure and properties of ceramic coatings.

Technical Description:

Feedstock powders are an important determinant of the final microstructure, properties, and wear resistance of coatings. Important powder characteristics include particle size distribution, chemical composition, phase content, flow, and thermal properties. This program attempts to develop a comprehensive understanding of the interrelationships among powder, deposition behavior, microstructure, and properties. This is accomplished by conducting a broad range of characterizations on a given powder or deposit.

Collaborative research is emphasized. The NIST effort focuses on powder characterization, while plasma spray deposition is conducted by others. The combined results are analyzed jointly to relate powder properties to process parameters, microstructure, and performance. Earlier research addressed the role of organic binders in zirconia feedstock on the thermal shock behavior of coatings and the role of particle size distribution on spray behavior. Subsequent research has been conducted in cooperation with a broad range of powder producers, plasma spray equipment and analytical instrument manufacturers, and coatings producers and culminated in the development of SRM 1982, yttria stabilized zirconia for thermal barrier coatings, for the calibration of particle size distribution measurement instruments. This research has been extended to the development of SRMs 1984 and 1985 for size distribution of tungsten carbide/cobalt feedstock used in the manufacture of wear resistant coatings.

External Collaborations:

This research is conducted in cooperation with the thermal spray industry, universities and government laboratories. Technical collaboration with organizations representing engine manufacturers, material manufacturers, spray equipment and instrument suppliers includes: Pratt & Whitney, General Electric, Caterpillar, Praxair, METCO, Zircoa, TAFA, Metech, H. C. Stark, Leeds and Northrup, Horiba, Sandia National Laboratory, Osram/Sylvania, and the State University of New York at Stony Brook.

Planned Outcome:

The planned outcome of this research is the development of analytical methods which will enable manufacturers to improve process control and deposition efficiencies, and material specifications. The product of this research is a Standard Reference Material (SRM).

Accomplishments:

Early research established an empirical relationship between organic binder content of spray dried and sintered yttria stabilized zirconia plasma spray feedstock and thermal shock resistance of coatings made from that powder. This work enabled tighter feedstock specifications by gas turbine manufacturers. Subsequent collaborative research culminated in the development of SRM 1982 – Zirconia Thermal Spray PSD for the calibration of particle size distribution measurement. Additional research in collaboration with Sandia has utilized SRM 1982 to determine the role of size fractions on behavior in the plasma spray process.

Feedstock research has encompassed development of small angle neutron scattering (SANS) techniques for the analysis of phase content in zirconia powder. This work has been extended to analysis of zirconia deposits. The SANS technique reduces the ambiguity associated with the presence of overlapping peaks observed with x-ray diffraction and allows measurement of phase contents critical to long-term stability of thermal barrier coatings.

In 1999, two additional SRMs for calibration of size measurement instruments were developed. SRM 1984, Tungsten Carbide/Cobalt for particle size distribution consists of a spherical, spray dried and sintered powder in the size range of 50 μm to 100 μm. SRM 1985, is a non-spherical fused and crushed material of a similar size distribution. Both of these SRMs are materials used by industry and represent the largest segment of the thermal spray industry.

Publication:

S. J. Dapkunas, "Measurement Methods and Standards for Processing and Application of Thermal Barrier Coatings," Journal of Thermal Spray Technology, Vol. 6 (1), 67-76 (1997).

PROGRAM TITLE: Ceramic Coatings

PROJECT TITLE: Database Development for Thermal Spray Coatings

Principal Investigators: Ronald G. Munro and Stanley J. Dapkunas

Technical Objective:

The objective of this project is to provide a focused collection of evaluated data on the thermal and mechanical properties of ceramic coatings.

Technical Description:

Ceramic coatings provide thermal insulation, wear resistance, and corrosion protection and allow components made from conventional materials to be used at temperatures higher than what the conventional material alone could usefully sustain. As a result, ceramic coatings extend the useful lifetime of the components and enable the application apparatus to be operated with a higher thermodynamic efficiency. Extensive applications of coatings are found in aircraft engines, stationary gas turbines, and diesel engines.

While the materials used for coatings may have the same nominal chemical composition as their counterpart bulk ceramics, the context in which the data for ceramic coatings are considered often differs from that of bulk materials because of the presence of an intermediate bond coat and a substrate and because of the dimensional and microstructural differences. Currently, there exists no publicly accessible, numeric property database relating to the special nature of ceramic coatings and their applications.

Planned Outcomes:

A database of evaluated thermal and mechanical property data relating to the characteristics and applications of ceramic coatings will be established. Data from an initial set of approximately 100 papers will be collected and evaluated during the first year of the project, and a mature database should be established within three years.

Accomplishments:

A preliminary study was conducted in FY1999 to examine the feasibility and usefulness of developing a materials property database for ceramic coatings. A sampling of the published literature, consisting of approximately 50 papers, was collected from a variety of journals. The papers were reviewed to determine what kinds of information were being reported or used and what data issues were considered to be the most important. It was found that greater attention was given to the material processing information than is commonly found in papers on bulk structural ceramics, but the range of properties needed for applications was essentially the same for the two types of ceramic materials. The most commonly reported mechanical and thermal properties of ceramic coatings were hardness and thermal conductivity. Hardness was often used

as an indicator of the quality of the deposition product (the coating), while thermal conductivity was used as an indicator of the effectiveness of the coating as a thermal barrier. It was also found that the experimental methods needed for the measurement of the properties of thin coatings often are different in important procedural aspects from those used for bulk ceramics. For example, indentations from conventional hardness measurements using a diamond indentor tend to penetrate the coating and engage the substrate, thereby invalidating the hardness measurement for the coating. Techniques using nanoindentation and instrumented indentation can be used to resolve this problem. While the nature of the test remains the same, the details of the application differ.

From this preliminary study it was clear that the information needed for ceramic coatings differs significantly in *content* from what is needed for bulk ceramics, and therefore an effort focused specifically on ceramic coatings was desirable. However, the *form* of the available information was not significantly different from that encountered with bulk ceramics. Hence, our previous work on bulk structural and superconducting ceramics has been adapted to the development of a database for ceramic coatings. Data collection for that database has been initiated with an emphasis on thermal barrier coatings. The primary focus is on the thermal and mechanical properties of yttria stabilized zirconia coatings, $(1\text{-}x)ZrO_2 \cdot xY_2O_3$, with the mass fraction of Y_2O_3 ranging principally from 6 % to 8 %.

PROGRAM NAME: Ceramic Coatings

PROJECT TITLE: Modeling of Coating Microstructure and Failure

Principal Investigators: Edwin R. Fuller, Jr., Andrew R. Roosen, Stephen A. Langer [Mathematical and Computational Sciences Division (891), ITL], Jay S. Wallace, and Tze-jer Chuang

Technical Objectives:

This research is designed to assist industry in developing new paradigms for elucidating micro-mechanical behavior — elastic, fracture, deformation, damage, and other nonlinear phenomena — in real and simulated microstructures of ceramic coatings. A technique for obtaining average linear response from selected microstructural regions is envisioned, thereby providing local and bulk properties. Predictions of response for simulated and digital representations of actual microstructures with subsequent comparison to measured properties are a primary goal. Efficient storage and microstructural representation techniques are to be developed. The goal is the development of a generalized set of tools, which all materials scientists can and will want to use.

Technical Description:

This research models the mechanics and physics of heterogeneous microstructures of ceramic coatings at the microscopic level and develops computationally efficient algorithms and computational codes for simulating the micro-mechanical behavior of these materials. New methods are developed to simulate concurrent physical phenomena in realistic coating microstructures. Elasticity and thermal-expansion-induced residual stresses in the complex microstructures of air-plasma sprayed thermal barrier coatings are explored via computer simulations on both actual and simulated microstructures. In particular, local elastic properties, including elastic anisotropy, and the influence of surface roughness and a thermally grown oxide interlayer on residual stresses are investigated. Fracture simulations in these microstructures have also been conducted, but this work is in the early stages. Here we seek to understand the influence of coating heterogeneities on the development of damage shear bands, which ultimately might lead to coating failure. Additionally, the project seeks to develop computationally efficient algorithms for simulations of the microstructural development in these materials.

External Collaborations:

This research involves numerous external collaborations. Informal joint projects include:

- Drs. Chun-Hway Hsueh and Paul Becher
  Metals and Ceramics Division, Oak Ridge National Laboratory, Oak Ridge, TN
  Collaboration on the influence of bond-coat roughness and the thermally grown oxide interlayer on residual stresses in air-plasma sprayed thermal barrier coatings.

- Stefan Lampenscherf, Manfred Bobeth, and Prof. Wolfgang Pompe,
  Institut für Werkstoffwissenschaft, Technische Universität Dresden, Dresden, GERMANY
  Collaboration in residual stresses and fracture simulation for model thermal barrier coating systems.Uwe Leushake and Prof. Dr. Wolfgang Kaysser
  DLR - German Aerospace Research Center
  Institute of Materials Research, Cologne, GERMANY
  Simulations to elucidate microstructural design of EB-PVD thermal barrier coatings.

- Robert Derr and Prof. Chuanshu Ji
  Department of Statistics, University of North Carolina, Chapel Hill, NC
  Collaboration in the development of new statistical tools for generating and quantifying microstructural features.

Planned Outcome:

A new paradigm for materials calculations is foreseen through the development of computational tools. These tools are envisaged as an inexpensive means by which industry can test and design coating microstructures.

Ceramic coatings contain *rich* distributions of pore shapes and orientations. Computer simulations with selected distributions of textured elliptical pores will lead to new understanding of the influence of pore morphology (elliptical aspect ratio) and pore texture (elliptical orientation) on average elastic behavior of coatings. Current understanding, based on effective medium theory, often over-estimates the effect since interaction terms between pores are not included.

Plasma sprayed coatings typically have a rough interface between the ceramic overcoat and the metallic bond coat. At temperature an alumina layer grows thermally at the overcoat/bond-coat interface. Computer simulations on actual and simulated microstructures will elucidate the nature of the residual stresses that result from these coating features, and how they influence coating reliability.

Accomplishments:

An object-oriented finite element code (*OOF*) was developed, and used to study both simulated and actual coating microstructures. Averaged elastic properties of thermal barrier coatings were calculated on a microstructural basis from digitized images and compared with experimental measurements. Computational simulations were performed on random regions from a micrograph of polished sections of an air-plasma sprayed zirconia coating. Both plan and section views were considered. Elastic properties were treated as orthotropic in the plane. Experimental measurements were performed via Hertzian indentation with a spherical indenter on an instrumented micro-hardness machine. The specimen area sampled for both the simulations and

the experiments was approximately 0.01 mm^2.

Simulation studies were conducted to elucidate the influence of pore morphology and pore texture on elastic average behavior. Thus far, elastic properties of media containing a random distribution of elliptical pores of varying volume fractions were examined. Effective Young's moduli were found to be independent of the bulk Poisson's ratio and effective Poisson's ratio were found to *flow* towards a common value at the percolation threshold.

During plasma-spraying, adherence of the ceramic overcoat is strongly dependent on roughness of the underlying metallic bond coat. However, the resulting interfacial asperities modify the residual stresses that develop in the coating system due to thermal expansion differences, and other misfit strains, and can generate stresses that induce progressive fracture and eventual spallation of the ceramic coating. For a flat interface, the residual stress is parallel to the interface, as the stress normal to the interface is zero. However, the residual stress normal to the interface becomes non-zero, when the interface has a rough morphology. Computer simulations were performed using ***OOF*** on an actual microstructure of a plasma-sprayed thermal barrier coating (TBC) to give an estimate of the localized residual stresses. Additionally, model TBC microstructures were examined to evaluate the manner in which the topology of interfacial asperities and the thickness of the thermally grown oxide influence residual stresses.

Computer codes were developed in collaboration with Prof. Chuanshu Ji and Robert Derr of the University of North Carolina, Chapel Hill, to generate simulated microstructures of plasma sprayed coatings and structural ceramics. Statistical aspects of these simulated microstructures are investigated via Markov Chain Monte Carlo tools.

Publications:

Chun-Hway Hsueh, James A. Haynes, Michael J. Lance, Paul F. Becher, Mattison K. Ferber, Edwin R. Fuller, Jr., Stephen A. Langer, W. Craig Carter, and W. Roger Cannon, "Effects of Interface Roughness on Residual Stresses in Thermal Barrier Coatings," J. Am. Ceram. Soc., **82** [4], 1073-1075 (Apr. 1999).

C.-H. Hsueh, P. F. Becher, E. R. Fuller, Jr, S. A. Langer, W. C. Carter, "Surface-Roughness Induced Residual Stresses in Thermal Barrier Coatings: Computer Simulations," in proceedings of the 5th International Symposium of Functionally Graded Materials 1998, edited by W. A. Kaysser, (Trans Tech Publications Ltd., Switzerland, 1999), Materials Science Forum Vols. 308-311, 442-449 (1999).

Tze-jer Chuang and Edwin R. Fuller, Jr., "Analysis of Residual Stress State in Thermal Barrier Coatings," in proceedings of ANSYS Users' Group Conference, Session 1, College Park, MD, June 10, 1999.

T.-J. Chuang and E. R. Fuller, Jr. "Analysis of Residual Stress State in Thermal Barrier Coatings." in Fracture Mechanics of Ceramics, Vol. 13, Eds. by R.C. Bradt, K. W. White, D. Munz, M. Sakai, and V. Ya. Shevchenko, (Plenum Press, New York, NY, 1999).

C.-H. Hsueh, P. F. Becher, E. R. Fuller, S. A. Langer, and W. C. Carter, "Analytical and Numerical Analyses for Two-Dimensional Stress Transfer," Mater. Sci. Eng., submitted.

Chun-Hway Hsueh and Edwin R. Fuller, Jr., "Residual Stresses in Thermal Barrier Coatings: Effects of Interface Asperity Curvature/Height and Oxide Thickness," Mater. Sci. Eng., submitted, September 1999.

Chun-Hway Hsueh and Edwin R. Fuller, Jr., "Residual Stresses in Thermal Barrier Coatings: Analytical Modeling of Oxide Thickness Effects," *Scripta Materialia*, submitted, September 1999.

Additionally, important outputs from this project are the computer code, ***OOF*** (Object-Oriented Finite Elements), and the associated on-line manual. Both are available on the Internet and can be downloaded from the NIST Center for Theoretical and Computational Materials Science (CTCMS) software archives. A short description of ***OOF***, a gallery of simulations, and links to the CTCMS archives are located at the URL address:

http://www.ctcms.nist.gov/oof/

The on-line ***OOF*** Manual is located at URL address:

http://www.ctcms.nist.gov/~langer/oof/Manual/Manual.html

and a paper copy is available as "The OOF Manual: Version 1.0, NISTIR 6256. "

PROGRAM TITLE: Ceramic Coatings

PROJECT TITLE: Processing/Microstructure Relationships in Ceramic Deposit Coatings

Principal Investigators: Andrew J. Allen and Gabrielle G. Long

Technical Objectives:

The objectives of this research are to develop techniques for the microstructural analysis of ceramic coatings, to characterize the anisotropic microstructure as a function of the process parameters, and to relate subsequent microstructural evolution both to the service conditions and to the coating properties.

Technical Description:

A combination of Porod small-angle neutron scattering (SANS) and multiple small-angle neutron scattering (MSANS) studies is being used to quantify the three void structures that govern the properties of plasma-sprayed ceramic deposits: anisotropic distributions of cracks within the splats and interlamellar pores between them, together with a wide size distribution of globular and large tetrahedral pores. The effects of several spray-process parameters and post-processing variables have been explored for both gray alumina and yttria-stabilized zirconia (YSZ), thick, self-standing, deposits. The microstructural effects are also being related to the mechanical and other coating properties. Methods are being explored to extend these studies both to thin deposits attached to substrates, and to ceramic coatings other than plasma-sprayed deposits.

External Collaborators:

H. Boukari, J. Ilavsky (formerly, Institute of Plasma Physics, Prague), University of Maryland, C.C. Berndt, A. Kulkarni and H. Herman, SUNY/Stony Brook, and A.N. Goland, Brookhaven National Laboratory, are collaborating with the Ceramics Division on the processing-microstructual relationships.

Planned Outcome:

Quantitative assessments will be conducted to show that the microstructures of plasma-sprayed ceramic deposits and other ceramic coatings can be controlled by the process parameters and how these microstructures respond to service life conditions.

Accomplishments:

Previously, a unique combination of anisotropic small-angle neutron scattering (SANS) Porod scattering studies and anisotropic multiple SANS (MSANS) has been developed at NIST to characterize and quantify the porous microstructures of thermal barrier coatings in the form of thick plasma-sprayed ceramic deposits. It has been possible to follow the different microstructural

evolution of the principal void components (intrasplat cracks, intersplat lamellar pores, and globular or tetrahedral pores) as a function of thermal annealing cycles (that mimic service conditions), spray process parameters, and powder feedstock morphology. The SANS/MSANS results have been further correlated with coating properties such as the anisotropic elastic constants and, by our collaborators at Stony Brook, with thermal conductivity. By linking properties and microstructure to spray-process variables, the spray deposition temperature has been identified as a potential control factor in determining long-term coating integrity and adhesion to the substrate, a concern expressed at the recent NIST Ceramic Coatings Metrology Industrial Workshop.

With our collaborators at Stony Brook, we have been extending our studies to coating systems other than plasma-sprayed yttria-stabilized zirconia thermal barrier coatings. For example, magnesium aluminate (spinel) deposits are of increasing interest as dielectric coatings in the electronics industry. Spinel coatings have been studied by both SANS/MSANS studies and x-ray computed microtomography, and the results correlated with thermophysical and dielectric measurements. Out of the two morphologies studied, the coatings deposited from fused and crushed powder have lower porosity and exhibit a higher thermal conductivity and dielectric constant than those deposited from sol-gel powder. Thermal barrier coatings deposited at relatively low temperatures using high-velocity-oxygen-fuel (HVOF) as the carrier gas have recently become of interest because they appear to have lower thermal conductivity than do equivalent conventional plasma-sprayed material. Thus, studies have now also commenceed on this system.

With support from the Advanced Technology Program, we have continued to exploit grazing-incidence or near-surface SANS studies for exploring how far the generic relationships between microstructure and process variables, and between microstructure and deposit properties, can be extended to thin coatings, less than 200 μm thick, on substrates. These studies, employing a purpose-built sample stage and a surface reflection geometry with the grazing angle just above the critical angle, have focussed first on thick deposit yttria-stabilized zirconia samples, already well-characterized by the MSANS and SANS methods discussed above, then on newly prepared thin yttria-stabilized zirconia deposits on steel substrates, and most recently on "unknown" yttria-stabilized zirconia industrial coatings.

Previously, we have shown that the apparent surface area of cracks and pores oriented perpendicular to the spray direction could be recovered to an accuracy of 10% to15% when an unknown sample is compared with a well-characterized sample under similar experimental conditions. Recovery of the anisotropy in the Porod surface distributions has been more of a problem, and addressing this issue has been a focus in our most recent experiments. By systematic variation of the measurement geometry, a better understanding has been attained of the interaction between the incident neutron beam and the coating surface. We have found that while a flat and smooth surface is needed for a well-defined incident beam geometry, the disordered nature of the splats in the deposit precludes the formation of a specularly-reflected beam. Instead, multiple scattering from within the sample results in a surface-tangent beam. This means that the angle of grazing incidence, θ_G, must be calibrated directly using the surface-tangent beam, rather than the previously assumed specularly-reflected beam making an angle of $2\theta_G$ with the incident beam

direction. This change in interpretation and calibration of the data means that the maximum coating depth probed in typical measurements is 200 to 250 μm, slightly thicker than previously thought. The mean depth being measured increases to about 40 μm, for a typical coating. Given that individual splats are typically 10 μm thick, this depth remains very representative of the microstructure within the coating, away from the surface. Use of this surface-tangent beam has allowed us to re-calibrate our data and improve our data correction procedures. For the first time, we have recovered anisotropic Porod surface orientation distributions to within ~ 15% for a sample previously characterized using a conventional SANS geometry. Furthermore, the multiple scattering giving rise to the surface-tangent beam offers the prospect that MSANS studies might be possible using a grazing-incidence geometry, and that some of the size and porosity information discussed above for the thick self-standing deposits may ultimately be obtainable for thin coatings on substrates.

Publications:

A.J. Allen and N.F. Berk; "Probing Porous Ceramics Using Small-Angle Scattering," Neutron News, **9** [2] 13-18 (1998). Also see 'Reply to Comment,' Neutron News, **10** [1] 26 (1999).

J. Ilavsky, G.G. Long, A.J. Allen, H. Herman and C.C. Berndt; "Use of Small-Angle Neutron Scattering for the Characterization of Anisotropic Structures Produced by Thermal Spraying," Ceramics-Silikaty (Czech journal), **42** 81-89 (1998).

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G. G. Long, S. Krueger and A. J. Allen; "Multiple Small-Angle Neutron Scattering", J. Neutron Res., **7** 195-210 (1999).

J. Ilavsky, G.G. Long, A.J. Allen, and C.C. Berndt; "Evolution of the Void Structure in Plasma-Sprayed YSZ Deposits During Annealing," Materials Science and Engineering A, in press. (1999).

A.J. Allen; "NIST Establishes a Microstructural Basis for Property Changes in Ceramic Thermal Barrier Coatings During Thermal Cycling," NIST Highlight, February 1999.

PROGRAM TITLE: Ceramic Coatings

PROJECT TITLE: Residual Stress Measurements

Principal Investigators: Grady S. White, Linda M. Braun, Albert Paul, and Lawrence H. Robins

Technical Objective:

The objective of this project is to develop measurement procedures, using micro-Raman and luminescence spectroscopy, to evaluate localized residual stresses that can control and influence mechanical, electrical, and optical properties of materials

Technical Description:

Raman spectra are generated by the interactions of light with phonon modes in the unit cell. Consequently, stress induced changes in unit cell symmetry or bond strengths will cause shifts in Raman peak position and intensity; changes in applied stress as small as 10 MPa can be detected through resultant Raman peak shifts. Stress can be quantified through calibration of material constants, i.e., phonon deformation potential values that relate peak position to strain. In a similar manner, stresses in alumina cause shifts in the Cr^{3+} luminescence lines. We have used both Raman and photoluminescence measurements to probe stresses/strains generated in thermal barrier coatings as a function of thermal cycling treatments. In addition, observed effects of polarization/stress interactions in Raman spectra are under investigation. As the first step in this area, the Raman model that relates polarization to peak intensity has been modified to reflect the absence of an analyzer in the experimental configuration.

External Collaborations:

Modeling the effect of stress on Raman spectra is being investigated in collaboration with Dr. Michael Bell of the naval Research Laboratory (NRL). Stress effects on the reliability of thermal barrier coatings (TBC's) are being examined with Dr. Michael Lance and Dr. Alan Haynes at Oak Ridge National Laboratory. Dr. Henry Prask of the NIST Reactor Division has also used neutron scattering techniques to evaluate the average residual stress in the TBC's.

Planned Outcomes:

This work is intended to provide a broad understanding of the basic physics underlying the use of Raman measurements to evaluate stresses in solids. In addition, the work on the TBC's is expected to provide specific understanding of the evolution of stresses in thermal barrier coatings and the relationship of the stress to development to microstructural evolution of the TBC's during thermal cycling.

Accomplishments:

Polarization Effects on Raman Peak Intensity

We have modified published Raman models that relate Raman signal intensity to light polarization orientation. This modification accommodates experimental configurations that do not have an analyzer in the light path. Our model provides quantitative agreement with experimental measurements for five Raman lines, encompassing both doubly degenerate and nondegenerate symmetries, in sapphire.

Thermal Barrier Coatings

We have measured Raman and ruby-line photoluminescence (PL) spectra in a series of TBC's to monitor stress evolution in the TBC's as a function of thermal cycling history. Twelve nominally identical specimens were made by plasma spraying zirconia on Rene 5 substrates coated with a NiCrAlY bond coat. Two of the specimens were retained in the as-received condition. The remaining specimens were subjected to increasing numbers of thermal cycles. All of the thermally cycled specimens were heated simultaneously in a box furnace. After predetermined numbers of cycles, two specimens were removed from the furnace. The thermal treatment consisted of cycling the specimens between 200 °C and 1150 °C. Both heating and cooling rates were 600 °C/h. At 1150 °C, the specimens were held for one hour each cycle. The thermal treatments resulted in two specimens undergoing each of the following number of cycles: as-received, one cycle, 10 cycles, 50 cycles, 100 cycles, 350 cycles. All of the specimens survived the thermal treatments intact. However, the coatings on both of the specimens exposed to 350 cycles delaminated within two days after being removed from the furnace. The delamination occurred at the boundary between the thermally grown alumina scale and the zirconia, leaving alumina and zirconia on both the substrates and the undersides of the coatings.

Raman spectra for all of the specimens were obtained at three positions on tops of all of the zirconia coatings. In addition, spectra were obtained from three positions on both the substrate and the underside of the TBC coating for each of the delaminated specimens. Five Raman lines were fitted to Lorentzian peaks for each measured spectrum. For measurements made on the top surface of the TBC's, each of the Raman peaks displayed a similar trend, although, as expected, each line behaved quantitatively differently from the others. Initially, there was a large change in position for each peak between the as-received specimens and those that had been exposed to one thermal cycle. Thereafter, the peaks continued to shift, although in lesser amounts, with subsequent numbers of cycles. Plots of peak position *versus* log (# cycles) were linear for all of the Raman lines. It may be significant that the as-received data usually fell on the same line for log (# cycles) = 0.01. It is possible that this effect may reflect the effects of temperature excursion during the plasma spray process.

The large shifts in Raman peak positions (e.g., 12 cm^{-1} to 22 cm^{-1}) reflect both the formation of residual stresses and migration of yttria to grain boundaries during the thermal treatment. Using only Raman spectra, it is not possible to differentiate between the two processes. However, published x-ray data provide a quantitative relation between yttria content and lattice spacing.

Consequently, we are in the process of combining x-ray results with the Raman data to attempt to separate out the effects due to composition from those due to residual stress formation.
Raman measurements made on the substrate and undersides of the TBC's on the delaminated specimens detected a large (> 5 cm^{-1}) shift between the zirconia left on the substrates and that on the underside of the coating. Since we expect, on average, that the yttria content should be the same in both sets of measurements, we interpret this change to be stress relaxation in the zirconia resulting from the delamination. An interesting feature of these measurements is that more stress relaxation appears to occur in the zirconia remaining on the substrate than in the zirconia on the underside of the TBC coatings themselves.

PL measurements made of the thermally grown alumina scale through the TBC gave surprising results. As with the Raman measurements, PL spectra were obtained at three positions for each specimen. For the as-received specimens, no PL signal was detected, consistent with the lack of any thermally grown scale layer. All subsequent measurements on thermally cycled material detected the presence of the ruby PL lines. However, the PL data do not show an increase in compressive residual stress in the alumina scale as the number of thermal cycles increases. Rather, the data show that, after one thermal cycle, there is a wide array of residual stresses in the alumina scale that ranges from slightly tensile to highly compressive. Subsequent thermal cycling greatly reduces the spread of residual stress values, but the median value appears to remain approximately constant. Measurements made on the substrate and the underside of the delaminated coatings showed that, on those specimens, the alumina experiences a small stress relaxation but that the final stress states on the substrate and on the coating were about the same.

At this time, several features of this work are ongoing. In particular, we are attempting to separate Raman peak shifts due to yttria content from those due to residual stress formation by coupling analysis of the Raman spectra to the x-ray measurements. Successful completion of this effort should allow us to quantify the stresses formed on the surface of the TBC's as a function of cycling treatment. We are also conducting microstructural analysis (optical, SEM, and TEM) of the TBC's. This information will be used to explain the observed narrowing of the range of stress values in the oxide scale as the number of cycles increases as well as to determine the cause of the spallation observed in the specimens exposed to 350 cycles.

PROGRAM TITLE: Ceramic Coatings

PROJECT TITILE: Vapor Pressure and Temperature Measurements for Physical Vapor Deposition

Principal Investigators: J. W. Hastie and D. W. Bonnell

Technical Objective:

This research develops and applies advanced measurement methods for the determination of partial pressures and temperatures pertinent to the very high temperature, reactive environments present in physical vapor deposition (PVD). Near-term focus is on measurement of data for thermal spray and electron beam processing of thermal barrier and wear-resistant coatings, principally ZrO_2-Y_2O_3 and WC.

Technical Description:

The absence of measured vapor pressure and other thermochemical data above most liquid ceramic systems arises from the lack of reliable measurement methods at temperatures beyond about 2000 K. The measurement problems arise mainly from the highly reactive nature of ceramic liquids and vapors. To obtain data under such conditions, non-intrusive, containerless techniques need to be developed. Earlier work in our laboratory led to the demonstration of a proof-of-principle for an essentially containerless approach to measuring vapor species in thermal equilibrium with liquid ceramics. The approach involves use of a high-powered short (20 ns) pulsed laser to provide a localized melting and vaporization of the sample. The vapor is allowed to expand under vacuum, leading to a molecular beam which then travels to a mass spectrometer for analysis. For the *in situ* measurement of temperature, for both the laser heated pool and plasma torch droplet cases, the approach developed involved measurement of emitted light over a range of wavelength and with spatial and temporal resolution.

External Collaborations:

Work on temperature measurements involves a joint NIST (F. Biancanello, S. Ridder, and other members of the Metallurgy Division; P. Schenck, Ceramics Division) and external (J. Craig, R. Parker and co-workers, Stratonics, Inc.) collaboration. Work on species pressure measurements has involved an international collaboration for the purpose of identifying and reducing sources of uncertainty, particularly those associated with the application of ionization cross sections to the conversion of mass spectral data to absolute partial pressures. This collaboration involves Dr. J. Drowart, Frei Universite, Brussels, Belgium and Dr. C. Chatillon, CNRS, Grenoble, France and the work is sponsored by IUPAC (Commission II.3 on High Temperature and Solid State Materials Chemistry).

Planned Outcome:

Major coatings manufacturers and users (principally General Electric and Pratt and Whitney) require basic data and new measurement methods for improved process understanding and control. Our assistance to industry in developing *in situ* temperature measurement methods and in providing vapor pressure, intermediate species identity, and thermochemical data for the liquid-vapor phase interaction will enhance industry's ability to improve their processes and products through process monitoring and models. A knowledge of species identities and partial pressures will also be of value to the further development (e.g. by Stratonics, and others) of particle imaging pyrometry where vapor interferences with the thermal emission can be a source of error.

Measurements of pressure and temperature data for ceramic liquids will have generic value in providing key reference points for testing widely used but previously untested estimation approaches for extrapolating lower temperature solid phase data to conditions well above the melting point. Thus the NIST-JANAF and IVTANTERMO thermochemical tables, for example, can be critically tested against such data and improved extrapolation approaches developed for a wide range of materials.

Accomplishments:

During the first year of this project, considerable progress was made in the needed development of new approaches to allow quantitative vapor pressure data to be obtained from mass spectral results. An *in situ* method for measurement of deposition rate was developed, together with a theory relating the rate, and mass spectral ion intensities, to species partial pressures. A key component of the gas kinetic theory relating deposition rate to vaporization flux is the angular distribution of the vapor plume emanating from a localized hot spot. For the pressure range of interest (typically 0.01 MPa to 1 MPa) this distribution is controlled by gas dynamic flow and a forward-peaked, rather than simple cosine, distribution can result. In order to measure this distribution two approaches were developed. First, a deposition rate monitor was installed in the mass spectrometer apparatus such that the monitor's angular position could be adjusted and the rate measured as a function of angle. Second, an optical reflectometry approach (developed by P. Schenck) was used to measure the thickness variation of the deposits as a function of angle. Both approaches gave similar results. The method was successfully tested on a known system, graphite, and then used to measure the vapor pressure of liquid ZrO_2 -Y_2O_3 at 4690 K. Further work is in progress to obtain data over a range of temperature and pressure.

The measurement of temperature involved two related areas. First, the measurement of temperature, coupled with the pressure measurements, required development of a novel high speed approach owing to the 20 ns time scale of the laser heating experiments. The method involved measurement of the spectral emission of the liquid pool and fitting the wavelength dependence to a Planck radiation relationship. The second area of temperature measurement involved determination of ZrO_2-Y_2O_3 droplet temperatures in an actual plasma spray torch (joint with the Metallurgy Division). For this purpose, the approach developed for the laser heating experiments was adapted for use in conjunction with a newly developed industrial two color particle imaging pyrometer. A small fiber-optic-coupled broad-band spectrometer was used to

observe the spray particulate plume simultaneously with the imaging pyrometer. By fitting Planck functions to the spectroscopic data, ensemble averages of the temperature of the particles, together with spectral interferences that might influence two-color measurements were obtained for a variety of spray conditions. Comparisons have shown that both methods are in good agreement, paving the way for commercial application of imaging pyrometry.

CERAMIC MANUFACTURING PROGRAM

Ceramic products are primarily produced by powder processing, where raw material powders are mixed with forming additives and shaped by various means into green bodies, which are then fired to the final, hardened state. Depending on the final application, some parts require machining in the green state and/or in the final hardened state. The manufacturing costs can vary greatly depending on the reproducibility and reliability of the process operations. Because ceramics are susceptible to brittle fracture, the manufacturing steps used in their production must be carefully controlled and/or monitored to ensure that the required properties are obtained. One key to reliable and rapid development of new products is the availability of established test methods to analyze the material at its different stages of manufacturing. Unfortunately, no satisfactory measurements infrastructure yet exists within the ceramics industry, and as a result, success of manufacturing operations relies largely on art and experience.

The objective of the Ceramic Manufacturing Program at the National Institute of Standards and Technology is to provide measurement techniques, standards, basic data, and predictive models needed by U.S. industry for cost- effective manufacturing of ceramics. Research activities include off-line and on-line measurement methods needed for processing of ceramic powders and suspensions, and for machining processes applied to ceramics. Present activities are focussed on measurements of particle and aggregate size and shape, characterization of particle suspensions and rheological properties of ceramic slurries, identification of the influence of powder characteristics and processing conditions on the resultant microstructures, homogeneity measurements on pre-sintered ceramics, and identification of machining induced damage and the influence of this damage on mechanical properties.

As an integral part of the Ceramic Manufacturing Program, NIST has initiated two unique government/industry/university partnerships. The Ceramic Machining Consortium was established in 1992 in response to a comprehensive survey of the U.S. advanced ceramics industry indicating that the high cost of machining and, at times uncertain reliability associated with machining damage were significant impediments to more widespread use of advanced ceramics. This Consortium is designed to address generic industry needs for improved machining technology to be utilized in the manufacture of reliable and cost-effective ceramic components. This is achieved primarily through the development of critical measurement methods, data, and standards. The Consortium members, representing a broad spectrum of industry consisting of materials producers, machine tool builders, suppliers of expendables (such as grinding wheels and fluids), and end users participate by providing materials, testing, and other in-kind contributions. The Consortium members also assist NIST in formulating the overall scope of the research projects and contribute to the detailed planning of related experiments. The close working relationship developed between industry, academic institutions, and NIST not only insures the relevance of the research projects but also promotes an efficient and timely transfer of research information to industry for implementation.

The Ceramic Processing Characterization Council (CPCC) was formed in 1997 to strengthen the measurement and standards infrastructure for the U.S. ceramic processing industry. The ultimate goal of the Council is to enhance the competitiveness of the U.S. ceramic manufacturing industry in the global market by reducing the processing costs and increasing the reliability of manufactured parts through implementation of efficient and reliable measurement methods and standards. The Council evaluates the measurements needed for all ceramic manufacturing processes, including powder characterization, powder processing, shape forming, characterization of green bodies, and sintering and densification processes. The Council provides a forum for establishing a dialogue between scientists in research laboratories and universities, manufacturers of analytical instruments, and engineers in industry involved in various manufacturing processes. The specific activities of the Council include:

- Periodic critical assessments of the available measurement methods and standards
- Identification of current and emerging measurement technologies
- Identification of needed measurement methods and standards
- Participation in round robin tests and analysis of data from such tests
- Development, dissemination, and fostering the use of standardized terminology
- Collection, validation, and publication of measured data

PROGRAM TITLE: Ceramic Manufacturing

PROJECT TITLE: Abrasive Finishing and Wear of Dental Ceramics

Principal Investigators: Said Jahanmir and Lewis Ives

Technical Objectives:

The use of ceramics for dental restorations has incresed in recent years due to their desirable aesthetics, good durability, and proven biocompatibility. The objectives of this research are to determine the influence of microstructure on abrasive finishing behavior and wear resistance of dental ceramics, and to assess the possible influence of machining damage on strength and wear of these ceramics.

Technical Description:

The conventional approach in preparing ceramic restorations, for example crowns, consists of first taking an impression of the clinically prepared tooth, and then preparing a mold, which is used to produce a casting of the restoration. The casting is then shaped to specified dimensions by grinding and polishing. As a final step, the dentist finishes the contacting surfaces with a dental handpiece to achieve a precise fit. This sequence of events is time consuming and expensive. In a recently developed procedure, the dental restoration is prepared by machining instead of casting. Application of machining to ceramics, however, requires data and information on machinability as well as on the effects of machining on strength, wear resistance, and contact fatigue. Most clinical failures of restorations have been observed to result either from processing defects in the material or damage produced by machining and/or wear. The specific tasks during this reporting period consisted of the following: (1) Influence of Microstructure and Properties on Abrasive Finishing with Dental Diamond Burs, (2) Relationship Between Microstructure and Wear Resistance, and (3) Effect of Machining Damage on Wear Resistance.

External Collaborations:

This project is part of a program funded at the University of Medicine and Dentistry of New Jersey by the National Institute of Dental Research to evaluate the relationship between the microstructure of dental ceramics and their performance with respect to machinability, wear resistance, and mechanical properties. NIST (S. Jahanmir and Lewis Ives, Ceramics Division and B. Lawn, MSEL) is participating in this program with the University of Maryland at College Park (Departments of Mechanical Engineering and Materials Science), and the University of Maryland at Baltimore (Department of Restorative Dentistry). In addition to the academic collaborators, two companies (Norton/Saint Gobain and Vita Zhanfabrik) participate by providing dental ceramics for the investigations. The overall program of which this project is a part is unique in that it brings together a diverse group of scientists and engineers with backgrounds in materials science, tribology, mechanical engineering, physics, chemistry, and dentistry. The group meets once a month to review results and plan future research activities.

These meetings are highly beneficial for cross-fertilization of ideas and transfer of information between the different disciplines. The team members participate in workshops and conferences related to their respective fields of expertise and report relevant information to their colleagues in the program. The companies that provide materials for research benefit by receiving data and information generated by the program for their internal use in the design of improved dental ceramics.

Planned Outcome:

This project will provide guidelines for microstructural design of dental ceramics to optimize performance based on wear of restoration and enamel, and guidelines for proper selection of machining parameters for use in abrasive finishing processes used by dental technicians and dentists.

Accomplishments:

The abrasive finishing response of a number of dental restorative materials used in practice to prepare crowns, bridges, and inlays was investigated. The materials included glass-infiltrated aluminas and spinels, a porcelain, and a yttria-stabilized zirconia. An instrumented apparatus incorporating a dental handpiece was used to conduct the finishing studies. With this apparatus it was possible to control the applied load, select coolant flow rate, vary burr rotational speed, and measure and collect data on grinding forces. Experiments were carried out with commonly used diamond grit burrs with grit sizes ranging from ultrafine (10 μm) to supercoarse (181 μm). Material removal rate, surface finish, and edge chipping were assessed under selected test conditions. The removal rate and the surface roughness increased substantially with increasing bur grit size. Similarly, edge chipping, which is closely associated with subsurface damage, was greater for coarse grit burrs than fine grit burrs. The amount of edge chipping for a given grit size, however, was a complex function of hardness, toughness, and microstructure. Among all the dental materials studied, the yttria-stabilized zirconia exhibited no measurable edge chipping.

Wear experiments were conducted using a pin-on-disk tribometer. In these tests the specimens were submerged in distilled water and the tests were conducted with parameters (e.g., load, speed, sliding distance, etc.) selected to simulate typical oral conditions. Examination of the wear scars on the samples and of the wear debris by scanning electron microscopy indicated that wear of porcelain based ceramics and the glass-ceramics was dominated by a microfracture mechanism. The glass-infiltrated alumina ceramics exhibited the highest wear resistance among all the materials that been tested in this project. The wear mechanism in this material consisted of a localized microfracture process along the glass/alumina interfaces.

In a series of tests conducted to simulate contact between a ceramic restoration and human enamel, hydroxyapatite pins were slid against the glass-infiltrated alumina. While the alumina sample exhibited a high wear resistance, the hydroxyapatite pin was subjected to a high rate of wear. In an series of experiments conducted to investigate the influence of machining damage and surface roughness on the wear behavior, it was found that the wear rate of hydroxyapatite increased almost linearly as the roughness of the alumina disk surface was increased. A similar

result was obtained when zirconia disks were used instead of alumina. These results clearly show the importance of controlling the final surface roughness of ceramic dental restorations, as rough surfaces can cause substantial wear and damage to the opposing natural enamel.

Publications:

H. H. K. Xu, D. T. Smith, S. Jahanmir, E. Romberg, J. R. Kelly, V. P. Thompson, and E. D. Rekow, "Indentation Damage and Mechanical Properties of Human Enamel and Dentin," Journal of Dental Research, 77 (1998) 472-480.

H. H. K. Xu and S. Jahanmir," Effect of Microstructure on Damage Tolerance in Grinding Micaceous Glass-Ceramics," Journal of Materials Research, 13 (1998) 2231-2236.

V. S. Nagarajan, B. Hockey, and S. Jahanmir, "Contact Wear Mechanisms of a Dental Composite with a High Filler Content," J. Mat. Science, (1999) in press.

X. Dong, L. Yin, S. Jahanmir, L. K. Ives, and E. D. Rekow, "Abrasive Machining of Glass-Ceramics with a Dental Handpiece," *Machining Science and Technology,* (2000) in press.

L. Yin, L. K. Ives, S. Jahanmir, E. D. Rekow, and E. Romberg, "Machining Behavior of Glass-Infiltrated Alumina," *Machining Science and Technology,* (2000) in press.

PROGRAM TITLE: Ceramic Manufacturing

PROJECT TITLE: Characterization of Pre-sintered Ceramics

Principle Investigators: Pu Sen Wang, Dennis Minor, Patrick Pei, and Lin Lum

Technical Objectives:

The objective of this project is to provide standard reference materials, data, and test methods for the measurement of density, porosity, moisture content, binder distribution, and internal defects in pre-sintered ceramics.

Technical Description:

Microstructure of pre-sintered ceramics has a major influence on properties and performance of ceramic products. As a part of the Ceramic Manufacturing Program, this project is responsible for exploring, identifying, testing, and evaluating potential measurement techniques for characterization of bulk density, porosity, moisture content, moisture distribution and diffusion, and binder content and distribution in pre-sintered ceramics. Standard reference materials required to calibrate instruments which measure these parameters will be developed. Interlaboratory round robin tests needed for the development of national and international standard test methods will be performed.

External Collaborations:

Corporate collaborators in this project include: AlliedSignal, General Motors, Pfaltzgraff China, Morganite Crucibles, Secondwave System, KDC Technology, Bruker Canada, Brimrose Corporation of America, Epsilon Industries, Zeltex and Micromeritics. These organizations have provided materials for testing as well as unique measurement methods not available at NIST.

Planned Outcome:

This project will provide fundamental information, evaluated data, standard reference materials and test methods for pre-sintered ceramic characterization for:

- Measurement of bulk density, porosity, moisture content, and binder distribution; and
- Correlations between processing parameters and homogeneity of green ceramics.

Accomplishments:

Several currently available moisture measurement techniques including gravimetric, near infrared, microwave, proton nuclear magnetic resonance, and magnetic resonance imaging methods were evaluated. Portable and table top near infrared spectrometers that can be installed on line were tested for moisture measurement with kaolin greenbodies containing a mass fraction of moisture ranging from 5% to 30%. The results were reproducible and both instruments are relatively low in cost and simple to operate. However, these measurements are limited by the penetration depth of

the light source and the results are influenced by the color of the samples. Microwave techniques allow for deeper penetration depths, without an influence from sample color. However, this technique has been found to have a limited accuracy for materials that contain impurities with dielectric properties comparable to that of water molecules.

Emerging NMR techniques were also tested for measurement of moisture content and distribution with alumina (content) and aqueous injection molded green bodies (distribution). The results showed that additional information, such as physical state of water and its spatial distribution in a ceramic sample are obtainable from these techniques. In the NMR imaging results, internal defects with high water concentrations were occasionally detected for injection molded greenbodies. The costs of these instruments are higher and the operational procedures are relatively more complex. They should be used as off-line research instruments. All the above techniques have to be calibrated with the gravimetric method (weight loss) to give absolute values of moisture content.

Green densities of cylindrical alumina compacts prepared by uniaxial pressing and square alumina tiles were investigated by mass-volume measurement, mercury pycnometry, powder displacement pycnometry, and noncontact (air coupled) ultrasonic methods. It was found that both mass-volume and powder displacement pycnometry techniques could determine the bulk densities of samples with well-defined geometries. The results were comparable to that of mercury pycnometry. The non-contact ultrasound (at 1 MHz) system was used to measure thickness, velocity, time-of–flight and attenuation of the test materials. The ultrasound velocity results measured for the samples were found to have a good correlation with the bulk densities obtained by pycnometric techniques.

A new activity was initiated this year to develop a standard reference material for calibration of Hg porosimeters for bulk density, pore size distribution, and pore volume measurements. The pore diameter detectable by this SRM ranges from 3 nm to 300 μm that are non-wetted by mercury. Several candidate materials were evaluated and a commercially available pre-formed porous ceramic was chosen based on the reproducibility of experimental results, cost, and ease of packaging and handling.

An international round robin measurement in green density and green strength of silicon nitride, silicon carbide, and aluminum oxide under the auspices of the International Energy Agency (IEA) has been completed. The green density of a simple shaped compact (cylinder) was obtained by taking the measured weight divided by the calculated volume (from measured dimensions). A comparison of test results from twelve laboratories showed that this method produced excellent repeatability and reproducibility. However, scattered data was observed when binder was removed. This probably is due to the inconsistent temperature of the furnaces and the length of the heating times in different laboratories.

Publications:

T. N. Wittberg and P. S. Wang, "XPS Study of the Dehydration of Clay and Kaolin Powders", *Surface and Interface Analysis*, **27**, 936-940 (1999).

P. S. Wang and G.Y. Onoda, "An Overview of Moisture Measurement Techniques for Ceramic Processing", Pages 263-278, *Advances in Process Measurements for Ceramic Industry*, edit. A. Jillavenkatesa and G. Y. Onoda, The American Ceramic Society Westerville, Ohio, 1999.

P. Pei, D. Minor, and G. Y. Onoda, "Laboratory Techniques for Bulk Density Measurement", Pages 293-305, *Advances in Process Measurements for Ceramic Industry*, edit. A. Jillavenkatesa and G. Y. Onoda, The American Ceramic Society Westerville, Ohio, 1999.

PROGRAM TITLE: Ceramic Manufacturing

PROJECT TITLE : Comparison of Powder Characterization Methods

Principal Investigators: Ajit Jillavenkatesa and Vincent A. Hackley

Technical Objective:

The objective of this project is to identify and establish underlying reasons for observed variations in results obtained when different techniques and instruments are used for powder size characterization.

Technical Description:

Over 400 instruments are commercially available that can be used for particle size and size distribution determination. Instruments based on different physical principles often exhibit a significant variation in the particle size and size distribution results for the same powder. These differences are prevalent even in instruments based on similar physical principles, but made by different manufacturers.

The goal of this study is to understand and identify the factors leading to these differences. Factors contributing to these differences will be classified as sample based or instrument based. Sample based parameters arise due to the nature of the powder being studied and to any steps in the sample preparation method. Instrument based parameters are inherent to the instrument and may be the result of algorithms used for data analysis, physical location of and type of instrument components etc. Particle size analysis instruments based on principles of laser light scattering, gravitational sedimentation, ultrasonics and microscopy will be the focus of this study.

External Collaborations:

The external collaborators include H. C. Spinks Clay Company, Inc., US Biomaterials Corporation and Ferro Corporation (Electronic Materials), who supplied well characterized industrial samples for testing using the slide dipping technique. Other collaborators on this project are the faculty members from the New York State College of Ceramics at Alfred University and the École Polytechnique Fédérale de Lausanne, Switzerland. These collaborations include size analysis and distribution determination using instruments and techniques not available at NIST.

Planned Outcomes:

This study is expected to result in the development of procedures and protocols for sample preparation and for the measurement of the size and size distribution of ceramic powders. Attempts will be made to develop formulae for correlating size distribution results from one technique to those obtained from another technique. These protocols will be developed initially for mono-sized spherical particles, and then may be extended to multi-modal powder systems, and systems with irregularly shaped particles.

From the size analysis results on the mono-sized spherical 1 μm silica powder a reference material (RM) may be developed. This powder will serve as a cross-platform size standard that can be used on various particle size analysis instruments.

Some of the results from this study will also help formulate information for a "Guide to Practice : Particle Size Analysis", a NIST publication designed to address common issues encountered in particle size and distribution analysis of ceramic powders.

Accomplishments:

A "model" powder system comprising of uniform mono-sized, spherical SiO_2 particles was identified as a suitable powder for this study. Preliminary studies focussed on physical, chemical and structural characterization of this powder. An understanding of these properties is essential to interpret any influences of these on the size distribution measurements. Inferences from measurement of density and surface area indicated a gradient in pore volume of the powders from the surface to the core. Such porosity distribution may effect the optical characteristics of the powder, a significant parameter for size characterization by laser light scattering. These powders were then characterized using optical and electron microscopy and size distributions of the powders obtained. These measurements will be used as baseline measurements for comparison of results from various size measurement techniques. Sample preparation procedures for dispersing these powders have been developed and used for analysis by laser light scattering. It was determined that creation of a stable, concentrated stock suspension of these powders was possible. Results indicated that dilution of the stock suspension to the desired concentration level and size determination gave results very similar to those for freshly prepared dilute suspensions. Various sample and instrumental factors that could influence the size distribution results were identified and examined. The role of pH in stabilization of the suspension, ultrasonication time, sample concentration, influence of real and imaginary components of refractive indices, levels of laser obscuration on the measured size and size distribution were addressed and determined. The size results from laser light scattering and microscopic studies were compared and found to be in close agreement. Studies are underway to study these particle by gravitational sedimentation based techniques.

While attempting to conduct microscopy based analysis, it was determined that conventional techniques for microscopy sample preparation were inadequate, as they would cause agglomeration of particles upon drying. Consequently, a specimen preparation technique was developed that enables preparation of slides with particles in a state of dispersion similar to that which exists in suspension. This technique has been found to be very effective for a wide range of powder systems with widely varying surface characteristics, a wide range of solids loadings and a broad size distribution.

Publications:

A. Jillavenkatesa and V. A. Hackley, "Identification and Characterization of a Model Powder System for Assessment of Powder Size Measurement Techniques and Procedures" in *Advances in Process Measurements for the Ceramic Industry* (American Ceramic Society, Westerville, OH, 1999) p 29.

A. Jillavenkatesa and G. Y. Onoda, Editors, Advances in Process Measurements for the Ceramic Industry (American Ceramic Society, Westerville, OH, 1999).

PROGRAM TITLE: Ceramic Manufacturing

PROJECT TITLE: Effects of Machining Damage on Properties of Ceramics

Principal Investigators: Lewis Ives, Said Jahanmir, George Quinn, and Patrick Pei

Technical Objectives:

The objective of this project is to assist industry in the development of abrasive machining and finishing technology for the manufacture of reliable and cost-effective components made from advanced ceramics. This is accomplished by providing data and measurement methods to assess the influence of damage produced by abrasive machining and finishing on properties and performance of ceramics.

Technical Description:

Abrasive machining and finishing processes are used extensively in the manufacture of a broad range of ceramic parts and components by a diverse group of industries including automotive, aerospace, medical, and electronics. Advancing the technology associated with abrasive machining and finishing processes is often cited as an important means for reducing manufacturing costs and improving the reliability of ceramic products. Also resulting from improvement in these processes are the likely increase in use and emergence of new applications for ceramic materials, taking advantage of their often unique and exceptional mechanical, thermal, chemical, and electronic properties. Active tasks during this reporting period consisted of the following: (1) Effect of Grinding Conditions on Strength of Cylindrical Rods, (2) Measurement of Inter- and Intra-Laboratory Strength Variations Associated with Grinding, (3) Development of a Standard Test Method for Assessment of the Effects of Machining Damage on Strength, (4) Influence of Finishing Methods on Strength and Contact Fatigue of Silicon Nitride and (5) Determination of Particle Size Distributions in Chemomechanical Polishing Slurries and their influence on removal rate and surface finish. These tasks were carried out jointly with members of the Ceramic Machining Consortium. The Consortium members provide in-kind contributions consisting of ceramic materials, diamond grinding wheels, sample preparation, and testing, as well as input on project selection and planning.

External Collaborations:

Industrial and academic organizations participate in this project by joining the Ceramic Machining Consortium and signing a CRADA for joint research on specific research tasks. The following is a list of organizations that were members of the Consortium during the past year: Cabot Corp.; Ceradyne, Inc.; Chand Kare Technical Ceramics; Milacron, Inc.; Ferro-Ceramic Grinding, Inc.; Ford Motor Company; General Electric Company; Heraeus Amersil; Landis / Western Atlas; Michigan Technological University; Norton Company; North Carolina State University; Stevens Institute of Technology; Torrington Company; University of Alaska; University of Arkansas; University of Delaware; University of Toledo; and West Manufacturing Technologies, Inc.

The members of the Ceramic Machining Consortium participate in joint research and have direct access to the data generated by the projects. The Consortium holds two meetings each year to review ongoing projects and plan future activities. The results generated by the projects are being used by industrial members to develop more cost-effective machining finishing methods, to design improved grinding wheels and formulate better grinding fluids, to develop new ceramic materials, and in general, to optimize their manufacturing operations.

Planned Outcome:

Four major outcomes are expected from this program: (1) recommendations for optimum selection of grinding parameters to be used for specific ceramic materials, (2) guidelines on finishing methods to obtain damage-free nano-precision surfaces on bearing grade silicon nitride ceramics, (3) guidelines for the assessment of particle size distributions and their influence on the behavior of chemomechanical polishing slurries and (4) recommended test procedures for the assessment of the effects of abrasive machining damage on strength.

Accomplishments:

A four point flexure test method for cylindrical rod specimens has been developed and used to evaluate the influence of several different grinding conditions on the strength of a structural silicon nitride material. Flexure test methods, using specimens of rectangular cross section, have been the predominant means for determining the flexure strength of ceramics. Guidelines detailing specimen dimensions, specimen preparation, and test procedures are given in ASTM standard C1161. This approach is directly applicable to flat surfaces. A great many—perhaps the majority—of manufactured components are cylindrical or have circular cross-sections. As a consequence, a clear need was identified by the Consortium to develop a test method for determining the influence of surface grinding on the flexure strength of cylindrical specimens. To accomplish this task, a new flexure test fixture for cylindrical specimens was designed and constructed. Initial design verification was accomplished by using strain gaged specimens and by conducting tests on fused silica specimens. The fixture has recently been used successfully to compare the effects of longitudinal and transverse cylindrical grinding on a silicon nitride material. Plans for future studies have been made to determine the influence of a number of important grinding parameters on the flexure strength of silicon nitride, silicon carbide and other structural ceramic materials.

A test program to determine both the experimental variability in flexure strength that might be expected to occur for specimens ground within a given machining facility and the variability that might occur between different facilities was completed this year. Previous round robin studies to determine the influence of grinding conditions on flexure strength had revealed the existence of relatively large experimental variations, both within the data of a single for a single facility and between different facilities. The just-completed test program was designed specifically to determine the extent of these variations and to reveal its source. Eight Consortium members participated directly in the program. Through careful control of all grinding parameters and conditions it was possible to obtain a statistical assessment of the size of the variations and to demonstrate that the main source of variation is associated with differences in the grinding

wheel. The magnitude of variation was found to be exacerbated by truing and dressing, but wear associated with normal use of the wheel was also a source of variation.

Development of a standard test method for the assessment of the effects of machining on the strength of advanced ceramics is currently underway under the auspices of ASTM Committee C-28 on Advanced Ceramics. The proposed test method is based primarily on the procedures developed and evaluated jointly with the members of the Ceramic Machining Consortium during the past several years. A preliminary draft of the standard was presented to Subcommittee C-28.05 for evaluation. Based on comments received, a revised draft has been prepared and will be submitted for subcommittee ballot.

Rolling contact fatigue life is well-known to be sensitive to the presence of surface flaws. An investigation of the influence of machining damage on rolling contact fatigue failure is currently being conducted by members of the Ceramics Machining Consortium. Test specimens of a hot-isostatically pressed silicon nitride were prepared using two different finishing methods: tribochemical polishing (Stevens Institute of Technology), and conventional bearing superfinishing (Torrington). The samples were characterized at NIST for surface roughness and form. The average roughness Ra of the samples finished by tribochemical polishing was less than 0.004 μm, while the roughness on samples finished by conventional finishing was about 0.027 μm. Rolling contact fatigue tests were conducted by Torrington Inc. The tribochemical polishing method resulted in a substantial improvement, giving an L_{10} life that was approximately four times higher than obtained with the conventional superfinishing method. Plans have been made to apply chemomechanical polishing to the same specimens in order to evaluate the influence of that finishing method on rolling contact fatigue.

A new project was initiated to investigate the relationship between particle size and shape distribution characteristics and chemomechanical polishing (CMP) response. Chemomechanical polishing is a critical step in preparation of smooth damage free silicon wafer substrates and in the planarization of coated semiconductor structures. The quality and consistency of performance of CMP depends on a number of process variables including the presence of a closely controlled particle size distribution in the CMP slurry. Particle characteristics and particle size distribution influence removal rate and surface finish. The presence of excessively large particles or agglomerates can cause scratches and introduce unacceptable subsurface damage. Preliminary measurements have been made to determine the size distribution of several alumina particle slurries and tests conducted with these slurries on silicon and silicon nitride surfaces to correlate distribution characteristics with removal rate and surface finish.

Publications:

L. K. Ives, S. Jahanmir, L. M. Gill, and J. J. Filliben, "Effect of Grinding on Strength of a Sintered Reaction-Bonded Silicon Nitride," Interceram, Vol. 47, No. 3, 168-173 (1998).

H. H. K. Xu, S. Jahanmir, and L. K. Ives, "Mechanisms of Material Removal in Abrasive Machining of Ceramics," Interceram, Vol. 47, No. 6, 380-385 (1998).

Machining of Ceramics and Composits, Said Jahanmir, M. Ramulu, and Philip Koshy, eds., Marcel Dekker, Inc., New York, (1998).

Said Jahanmir, Hocken H. K. Xu, and L. K. Ives, "Mechanisms of Material Removal in Abrasive Machining of Ceramics," in *Machining of Ceramics and Composits*, Said Jahanmir, M. Ramulu, and Philip Koshy, eds., Marcel Dekker, Inc., New York, 11-84 (1998).

Philip Koshy, Lewis K. Ives, and Said Jahanmir, "Simulation of diamond-ground surfaces," International Journal of Machine Tools and Manufacture, Vol. 39, 1451-1470 (1999).

P. Hryniewicz, A.Z. Szeri, and S. Jahanmir, "Coolant Flow in Grinding with Non-Porous Wheels" International Journal of Mechanical Sciences, (in press).

PROGRAM TITLE: Ceramic Manufacturing

PROJECT TITLE: Interlaboratory Evaluation of Powder Characterization Methods

Principal Investigators: Lin-Sien Lum and Said Jahanmir

Technical Objectives:

The objectives of this project are to evaluate test methods for the characterization of selected properties of ceramic powders through an international round robin study and to determine the repeatability and reproducibility of the test methods. The results of this study will be used to develop recommendations for drafting of national and international standard test methods.

Technical Descriptions:

This project is being conducted under the auspices of the International Energy Agency (IEA). The goal of this activity, IEA Subtask 10, is to use the results of this international collaboration in drafting standard test methods in each participating country and through ISO. The properties that were measured during this phase of the project consisted of: (1) characterization of powders suspended in water (particle dispersion and rheology); (2) characterization of spray dried powders (flow rate, particle size distribution, moisture and binder content); (3) green body evaluation (bulk density and green strength). Three powders were studied: silicon nitride, silicon carbide and aluminum oxide in both the as received and spray dried granule form. Each participating laboratory used the same pre-defined procedures for each measurement. The compiled data were analyzed to determine the repeatability of the data within each laboratory and to examine variations in the data obtained by different laboratories.

External Collaborations:

Technical collaborations included participants form the U.S., Belgium, Japan, Germany and Sweden. The participating laboratories represent industrial, academic and government research organizations. There were overall thirty-four participants in the round robin study. The U.S. participants included Allied Signal, Micromeritics, OSRAM Sylvania, Trans-Tech, Alfred University and Sandia National Laboratories

Planned Outcomes:

This project will provide recommendations and guidelines for measurements and characterization methods applied to ceramic powders. It is planned to prepare NIST reports entitled "Guides to Practice", to provide general guidelines for the use of common measurement techniques for the characterization of particle size and size distribution of ceramic powders. The results of this international collaboration will be used to establish national and international standard test methods.

Accomplishments:

The international round robin study on properties of advanced ceramic powders has been completed. The compiled data were analyzed to determine the precision of each of the measurement methods.

The influence of ultrasonication on the state of dispersion of ceramic powders during particle size measurement was assessed. The method involves following the changes in the particle size distribution as a function of the ultrasonication time used to disperse the powder in dilute suspension. The results from the round robin indicated that the measured diameter of the particles decreased as the ultrasonication time was increased. The longest ultrasonication time (128 s) helped to eliminate potential errors associated with this dispersion procedure. The results also indicated that the preparation procedure should be re-examined and the dispersion parameters should be tightened.

Specific testing procedures were prepared to determine the flow rate, particle size distribution and moisture and binder content of spray dried powders. The round robin data indicated that the flow rate measurement procedure showed excellent repeatability and reproducibility values for the silicon nitride powder. The silicon carbide powder however showed inconsistent results; this lead to the suggestion for additional sample preparation procedures that are specific to the powder. The method used for analysis of the data for the measurement of the size distribution of the spray dried granules by sieving was the source of the scatter of the data between the labs. A better data analysis method is needed to determine the statistical variations and precision values. The data for the round robin study using the measurement method for moisture content showed excellent precision values for the silicon nitride powder. Further improvements are needed for the sample preparation for the silicon carbide powder. The round robin data for the binder content measurement method also showed excellent repeatability and reproducibility values for the silicon nitride powder. There was scatter in the data for the silicon carbide powder. This is due to the inconsistent and incomplete binder removal. The suggestion for improvement for this method includes additional work to improve the binder removal for the silicon carbide powder.

The participants of the round robin determined the bulk density of the green body compacts and measured the strength of green compacts using diametral compression tests. The data for the measurement of green strength exhibited good repeatability within the labs for the three powder compacts. Data scatter was observed from lab to lab for the silicon carbide and aluminum oxide compacts. The inconsistent results were due to the variations in the compact microstructure and the testing procedures.

Plans for continuation of this project are underway. The objectives will be similar to Subtask 10 except that the focus will be directed towards the characterization of green (pre-sintered) ceramics. Some of the measurements from Subtask 10 that require further evaluation are: rheological properties, particle size distribution of slurries, moisture content of granules, density and strength of green ceramics. There are also new measurements that will require drafting of new procedures: density gradients in green ceramics, porosity and pore size measurements, influence

of machining damage of strength of green ceramics and distribution of binders in pre-sintered ceramics.

Publications:

L.H. Lum, R. Gilissen, K. Meyer, M. Naito, H. Abe, R. Pompe, S. Jahanmir, "Assessment of Powder Characterization Methods for Advanced Ceramics", Final Report Subtask 10, International Energy Agency--Annex II, Co-Operative Programme on Ceramics for Advanced Engines and other Conservation Application, DOE Report (Jan. 2000)

PROGRAM TITLE: Ceramic Manufacturing

PROJECT TITLE: Particle Dispersion Measurements

Principle Investigators: Vincent A. Hackley

Technical Objective:

The objective of this project is to assist industry in the development of dispersion technology for cost-effective and reliable manufacturing of advanced ceramic components. This is accomplished by providing in-process and off-line measurement methods, process models, standards, uniform nomenclature and data.

Technical Description:

The manufacturing of advanced ceramics for the automotive, aerospace, power generation, and electronics industries typically begins with the dispersion of fine particulates at high concentrations in a liquid medium. These suspensions or "slurries" are used as vehicles to obtain homogeneous dense compacts, films or coatings, which are subsequently fired. One of the primary sources for defects in manufactured components can be traced to poor or inadequately controlled dispersion during the shape forming or coating process. Dispersion measurements are therefore critical to improving the cost and reliability of advanced ceramic processing. This project addresses a broad range of issues related to the development of better dispersion technology for the ceramics industry, including the application of ultrasonic-based sensors for in-process measurements, development of international standards and uniform nomenclature, and the acquisition of critical data through basic research activities.

External Collaborations:

Technical collaborations with external organizations include BAM (Germany), JFCC (Japan), Changwon National University (South Korea) and the Industrial Process Control Sensor Systems (IPCoSS) Program at the University of Maine. Additional cooperative activities have involved members belonging to the Ceramic Processing Characterization Consortium (CPCC) and the International Union of Pure and Applied Chemistry (IUPAC).

Planned Outcomes:

Major outcomes expected from this project are: (1) Improved methodologies and recommended test procedures for rheological and ultrasonic measurements in concentrated suspensions; (2) Specification, development and implementation of infrastructure for real-time monitoring and process control using ultrasonic-based sensors; (3) Published nomenclatures for the ceramic industry; (4) Improved methodologies for dispersion of submicrometer particulates in concentrated slurries.

Accomplishments:

Significant progress was made on the development of uniform nomenclature for the ceramics community. A *Guide to the Nomenclature of Particle Dispersion Technology for Ceramic Systems* was completed in cooperation with members of the CPCC-Dispersion & Rheology Project Group and IUPAC. This cooperation included technical contributions and critical reviews by select members of these two organizations. The *Guide* is organized into five technical areas: physical description of dispersed systems, states of subdivision, association and disassociation processes, dispersion stability, and interfacial and electrokinetic properties. A work-in-progress version of the Guide was distributed to consortium members as a CPCC Technical Note; the final version will be distributed as a NIST Special Publication. The second in a series of planned nomenclature guides specifically targeted toward the ceramics industry, focuses on rheological measurements in particulate suspensions and is currently in an early draft.

A two year joint research effort was completed under the Korean-U.S. Cooperative Science Program (supported by the Korea Science & Engineering Foundation in conjunction with the National Science Foundation). Collaborative studies were carried out with the research group of Dr. Ungyu Paik, then at Changwon National University, on measurement and control of interparticle forces in slurry formulations for processing of electronic ceramics. We determined, among other findings, that barium solubility significantly impacts the interfacial electrochemical properties of concentrated aqueous $BaTiO_3$ slurries for MLCC applications. We also found that conventional measurements in dilute suspensions may not accurately reflect the electrical properties of concentrated slurries due to solubility effects. A summary of all significant findings is currently being prepared for publication in a peer reviewed journal.

A new focus area was initiated this past year in cooperation with Dr. Hemant Pendse, chair of the Industrial Process Control Sensor Systems (IPCoSS) Program at the University of Maine, on in-process measurements for concentrated slurries. The purpose of this joint effort is to develop methodologies and measurement infrastructure for in-process ultrasonic-based sensing of complex industrial slurries for broad-based materials applications. Initial studies examine the feasibility of using electroacoustic and acoustic "soft" sensors in combination with other measured process parameters and material properties in order to develop an intelligent in-process control system based on neural-network technology. Future studies will focus on developing the necessary fundamental understanding and empirical correlations between sensor input and slurry properties. In support of this effort, a centralized electronic repository is being developed that will provide open access to information regarding terminology, published works, instrumentation and methodology, and critical data. The repository, a work in process, is located on the world wide web at *www.ceramics.nist.gov/ultrasonics/index.htm*.

A new joint effort on international standardization was begun at the end of FY99 and is funded by the Japanese New Energy and Industrial Technology Development Organization (NEDO). The objective of this effort is to propose several ISO standards for fine ceramics through joint studies with representative measurement laboratories in Germany (BAM) and Japan (JFCC). The NEDO effort recognizes that microstructural flaws typically originate in the earliest stages of the ceramic manufacturing process, often as a result of poor dispersion of the starting powders. In aqueous

systems, the state of dispersion is largely dependent on the electrical properties of the particle-solution interface. Electrokinetic measurements are the most convenient and established means for characterizing the electrical properties of slurries. To this date, however, no standard test procedure exists for the electrokinetic evaluation of ceramic suspensions. Standards are needed for industry to fully implement these techniques in a consistent manner. The goal of our research in the NEDO effort will be to cooperate with BAM and JFCC in laying the technical framework for developing these crucial standards. Our focus will be on methodology for characterizing the zeta potential and isoelectric point of fine ceramic suspensions using electroacoustic measurements.

Publications:

U. Paik, V. A. Hackley, S. Choi, and Y. Jung, "The Effect of Electrostatic Repulsive Forces on the Stability of BaTiO3 Particles Suspended in Non-Aqueous Media," *Colloids Surf. A: Physicochem. Eng. Asp.*, **135**, 77-88 (1998).

V.A. Hackley, and J. Texter, "International Workshop on Ultrasonic and Dielectric Characterization Techniques for Suspended Particulates," Conference Report, *J. Res. Natl. Inst. Stand. Technol.*, **103**, 217-223 (1998).

V.A. Hackley, and J. Texter, Editors, *Handbook on Ultrasonic and Dielectric Characterization Techniques for Suspended Particulates*, American Ceramic Society, Westerville, OH, 1998.

U. Paik, V.A. Hackley, and H. Lee, "Dispersant-Binder Interactions in Aqueous Silicon Nitride Suspensions," *J. Am. Ceram. Soc.*, **82**, 833-40 (1999).

V.A. Hackley, "Development of Electroacoustic Methods and Their Application in Ceramic Processing," pp. 237-259 in *Advances in Process Measurements for the Ceramic Industry*, Edited by A. Jillavenkatesa and G.Y. Onoda, American Ceramic Society, Westerville, OH, 1999.

PROGRAM TITLE: Ceramic Manufacturing

PROJECT TITLE: Standard Reference Materials for Powder Characterization

Principal Investigators: James F. Kelly, Patrick Pei and Dennis Minor

Technical Objectives:

The primary objective of this work is to develop and certify glass/ceramic powders as particle size distribution (PSD) and specific surface area Standard Reference Materials (SRM). These SRMs are needed in industry for instrument calibration, quality control in powder manufacture, and for compliance with ISO 9000 requirements. A necessary adjunct to this certification is the development of sampling protocols and size measurement procedures.

Technical Description:

Initial work in the development of these SRMs is the selection of a powder material with the desired chemical and physical characteristics such as size, shape, durability, and reactivity. Industrial sources of powders are identified, test powders evaluated, and production specifications developed in cooperation with the powder manufacturer. Procedures have been developed for splitting and bottling of the powder to achieve the necessary level of sample to sample homogeneity. The instrumental techniques utilized for the particle size measurements include optical and scanning electron microscopy, laser diffraction, sieving, sedimentation and electrical zone sensing. The primary techniques are the microscopies because of the direct calibration with NIST line standards.

External Collaborations:

The size distribution certification for the thermal spray materials included a round robin study by laser light scattering method with industrial participants from powder users, producers and instrument and equipment manufacturers. The participants were: OSRAM Sylvania, P/M Lab of the Pennsylvania State University, Sandia National Labs, Sympatec Inc., Dirats Laboratory, Stellites Coatings, TAFA Material Technology Inc., Honeywell Microtrac, TSI/Amherst, Horiba Instruments Inc., Duke Scientific Corp. and Beckman-Coulter.

As part of the development of an ASTM C28.05 test standard for elemental analysis using high temperature combustion instruments, a round robin study has been conducted with the following laboratories; LECO Corp., Horiba Instruments Corp., and St. Gobain Industrial Ceramics.
During the past year, cooperative research has taken place between NIST and BAM (Federal Institute for Materials Research and Testing) in the testing of several RM's issued by BAM. These materials included both specific area RM's and a porosity RM. Further cooperative research work will be conducted during FY 2000.

Planned Outcomes:

Our objective in this program is to carry out the research and development necessary to offer world class reference materials to U.S. industrial laboratories and test facilities. The primary standards for particle size distribution are a series of glass bead SRMs covering the range from micrometer to millimeter. Maintaining and improving these references is an ongoing effort. Requirements have been identified for several industry specific particle size distribution standards.

Representatives from manufacturers and end users of zeolites have identified three zeolite materials, which would be useful to them as reference materials. The Ceramics Division will provide the particle size distribution measurements of these materials while other laboratories at NIST will measure elemental composition and other material properties.

Development is underway for the certification of the 10 μm to 50 μm glass bead SRM 1003c. This is an important standard for industries using granular material. The certification analyses will use SEM, laser diffraction and sieving. A new SRM 1021 has been proposed, which will extend the lower range of available glass sphere size distributions standards to 1 μm.

During the spring of 1999 questions arose as to the stability of specific surface area (SSA) RM-8572 when several outside laboratories reported to NIST the results of their calibration activities using a batch of this material that had been in storage at NIST. Several samples of this material were tested by the Ceramic Manufacturing Group using testing protocols developed for the issuance of SRM's 1899 and 1900, nitrogen BET surface area SRMs. Significant differences were found between the certified value for SSA and the experimentally derived value for this material and the Standard Reference Program has withdrawn it from stock. These differences agreed with the reported values from the original reporting laboratories. The change in the value appears to be due to (re) agglomeration of the silica-alumina material over a prolonged period of time. RM-8572 will be rebottled, re-analyzed and certified during the year 2000 with a laboratory round robin testing program to take place during 2001. A storage and shelf life protocol will be issued with the new RM.

Accomplishments:

Spherical glass SRM's 1003b(10 μm to 60 μm), 1004b(40 μm to 150 μm), 1017b(100 μm to 400 μm), 1018b(220 μm to 750 μm), and 1019b(750 μm to 2450 μm), covering particle size ranges from 10 μm to 2450 μm, are now available to industrial laboratories and test facilities. This year a new SRM 1004b was produced. A special order of borosilicate glass beads were purchased with material specifications designed to obtain a product with an approximate lognormal mass versus diameter distribution with a mean diameter near 80 μm, a density of about 2.2 g/cm^3, and a refractive index between 1.47 and 1.48. The cumulative volume (mass) distribution was determined using both scanning electron microscopy (SEM) and standard sieving procedures. The certified values are based on the SEM/Image Analysis measurement of over twenty thousand individual beads using a microscopes calibrated to a micrometer slide measured at NIST using laser interferometry.

WC/Co SRMs1984/1985:Three bulk powders from different manufacturers were purchased, riffle split and bottled. Test bottles were analyzed by sieving, laser light scattering and SEM. Analysis protocols were established for the two light scattering instruments and the SEM. The two most suitable powders were selected for certification as SRMs. Measurements were made using SEM/Image Analysis, sieving, and laser diffraction techniques. A round robin test program was completed with laboratories representing equipment manufacturers, powder manufacturers, and end users. These two new WC/Co SRMs will complement the previously certified zirconia powder standard, SRM 1982.

The particle size measurements for zeolite SRM 2850, SRM 2851, and SRM 2852 were made using a laser based light scattering system. The powder to be measured was circulated through a glass cell where it interacts with a beam of laser light. Both Mie and Fraunhofer light scattering theories were applied to analyze of the pattern of diffracted light measured by an array of diode detectors. The analysis is able to calculate size distributions for particles in the range of 0.04 μm to 2 mm. The calculations depend to some extent on knowledge of the optical properties of the particles. Specifically, the real and imaginary components of the refractive index. For particles much larger than the wavelength of the laser light, the Fraunhofer diffraction theory can be used and is independent of the refractive index. The effect on the calculated size results of using different optical models was studied to determine the variation in PSD with several optical models. For a given optical mode, the PDS is very reproducible. A comparison of the light scattering results with x-ray sedimentation results was carried out for each of the three SRMs. Approximately 600 units per year of the size distribution standards are purchased by industry for use in their quality control and calibration programs.

Chemical impurities affect the agglomeration and sintering mechanisms of ceramic powders during manufacturing processes. To ensure high quality and reproducibility, both metallic and non-metallic impurities in the ceramic powder must be controlled. The three important non-metallic elements that are of interest in the processing of silicon nitride powders are nitrogen as a major element, carbon and oxygen as minor elements. At this time, these elements are determined quantitatively by analytical instruments and the accuracy is dependent on both the availability of calibration standards and standardized experimental procedures. RM 8983, silicon nitride powder for nitrogen, carbon and oxygen will provide the needed calibration standards and the development of an ASTM standard will also provide the necessary experimental procedure. RM 8983 is in the final process of being issued and the ASTM standard for the experimental procedure is being proposed to ASTM Committee C-28.05.

Publications:

SRM 1004b, Glass Beads – Particle Size Distribution, NIST Standard Reference Materials Program (in preparation)

SRM 1984, Tungsten Carbide Thermal Spray Powder – Particle Size Distribution, NIST Standard Reference Materials Program (in preparation).

SRM 1985, Tungsten Carbide Thermal Spray Powder – Particle Size Distribution, NIST Standard Reference Materials Program (in preparation).

James F. Kelly, "Powder Standard Reference Materials", 57-68, Advances in Process Measurements for Ceramic Industry, The American Ceramic Society Westerville, Ohio, 1999.

CERAMIC THIN FILM MEASUREMENTS AND STANDARDS

Functional ceramics (e.g., ceramics primarily intended for optical, electronic, or thermal management applications) are increasingly being used in film geometries. In response to this growing segment of the ceramics community, the Thin Film Measurements and Standards Program endeavors to provide improved measurement tools and data that are needed to evaluate advanced ceramic films and film systems. Increasingly, critical film performance requirements (e.g., reduced dimensions, increased purity, improved interface properties, increased production rates, and tighter control of properties) place stringent demands on film processing control, models, and characterization techniques. However, lack of measurement methods to monitor film processing and accurately characterize film properties as well as limited theoretical understanding of interrelationships between processing conditions and final film properties reduce most film processing to empirical procedures. The activities in this program are designed to address these measurement and modeling issues, both with regard to specific, near term industrial needs as well as to the development of a materials science knowledge base required for use of ceramic films in future applications. Near term and long range goals have been developed based upon both general discussions between Materials Science and Engineering Laboratory staff and representatives of industry and universities at professional meetings and consortia workshops, as well as focused, collaborative research projects with specific organizations.

The film characterization techniques in use or under development include electrical, mechanical, optical, thermal, and x-ray measurements. Specific research activities include:

- investigations of the processing and microstructural features that control poling behavior and domain stability in ferroelectric films;

- development and utilization of spectroscopic procedures to evaluate film composition and thickness, and to detect defects in ferroelectric and semiconductor films;

- development of methods to measure and statistically analyze texture and texture distributions in films and to relate these data to processing conditions;

- development of measurement procedures, models, and standards to permit quantitative evaluation of thermal diffusivity in thin films and to relate thermal diffusivity to film microstructure and morphology;

- application of advanced x-ray measurement capabilities (e.g., EXAFS, DAFS) to the analysis of film structure and composition, and the construction of an in-house state-of-the-art x-ray facility;

- development of standard measurement procedures and standards for determining film adhesion;

- participation in development of optoelectronic film composition standards for industrial photoluminescence and x-ray instrument calibration

A critical requirement for the projects cited above is the ability to generate model film systems. To this end, this program includes three film deposition capabilities: metalorganic chemical vapor deposition, metalorganic decomposition, and pulsed laser deposition.

PROGRAM TITLE: Ceramic Thin Film Measurements and Standards

PROJECT TITLE: Chemical Standards for Optoelectronics

Principle Investigators: Lawrence H. Robins, Albert Paul

Technical Objective:

The objective is to quantify and improve the accuracy of optical measurements, in particular photoluminescence (PL) spectroscopy, which are widely used to determine the chemical composition of ternary and quaternary compound semiconductor films. We are focusing on the technologically important $Al_xGa_{1-x}As$ and $In_xGa_{1-x}As_yP_{1-y}$ alloy systems. This project is part of the Compound Semiconductor Composition Standards (CSCS) Program, an ATP-supported effort by four NIST research divisions to develop high-accuracy, direct composition measurement methods based on chemical microanalysis, and produce standard reference materials with certified compositions in the selected alloy systems. Quantifying the accuracy of the indirect, optical methods, which are likely to remain the "first-line" methods of choice for industry due to their low cost and simplicity, is an important part of the CSCS program.

Technical Description:

Compound semiconductor manufacturers currently rely primarily on two indirect methods to measure the chemical composition of semiconductor alloy films: photoluminescence (PL) spectroscopy, and x-ray diffraction (XRD) rocking curves. These methods are referred to as indirect because the measured quantities, electronic band gap and lattice constant, are functions of composition, but may also vary with other factors such as temperature or strain. In this project, we will use PL spectroscopy to measure the band gap of samples provided through the NIST composition standards program. We will quantify the accuracy limits of the PL measurements by conducting internal and external round-robin comparisons of preliminary composition reference samples, conducting in-depth studies to resolve discrepancies, and applying related techniques such as cathodoluminescence to reduce uncertainties in the measurements. Specific factors to be addressed are wavelength accuracy, wavelength-dependent spectrometer response correction, peak fitting methods, excitation intensity, sample temperature, low level impurities, and, for $In_xGa_{1-x}As_yP_{1-y}$, residual strain.

To date, the CSCS Program has been directed toward the $Al_xGa_{1-x}As$ system, with $In_xGa_{1-x}As_yP_{1-y}$ growth expected to begin in the next year. XRD is of limited use for composition measurements in $Al_xGa_{1-x}As$ because of the very small lattice mismatch between the endpoints, but is expected to be more useful in the $In_xGa_{1-x}As_yP_{1-y}$ system.

External Collaborations:

The principal investigators from other NIST divisions in the CSCS Program are Kris Bertness, Optoelectronics, Joseph Pellegrino, Semiconductor Electronics, and John Armstrong, Surface and Microanalysis Science. Bertness and Pellegrino have the tasks of sample preparation and *in situ*

composition characterization, such as reflection high-energy electron diffraction (RHEED). Armstrong's task is developing high-accuracy composition measurement methods based on chemical microanalysis, in particular wavelength-dispersive x-ray spectroscopy in an electron microprobe (WDS).

Planned Outcomes:

Improvements in experimental techniques and/or data analysis methods will be developed that reduce the uncertainty and systematic errors in the measurement of the PL peak energy (the photon energy at which emitted intensity is maximum), or other well-defined "marker" energies within the PL emission spectrum. These improvements will be demonstrated as reductions in the discrepancies between measurements of the same sample conducted in different laboratories.

By utilizing the results of direct, chemical microanalysis based, composition measurements of the same samples investigated by PL, we will provide calibration values of the PL peak (or other "marker") energy at several known compositions. We will also provide a best-estimate calibration curve, giving the PL energy as a continuous function of composition, by linear or non-linear interpolation between the calibration points. For the more complex $In_xGa_{1-x}As_yP_{1-y}$ alloy system, with two composition variables, we plan to provide PL calibration values at several points within the two-dimensional composition plane. The latter outcome is dependent on the development of direct composition measurement methods for $In_xGa_{1-x}As_yP_{1-y}$.

The improvements in PL analysis and the generation of calibration curves will provide U.S. compound semiconductor industries with information needed to improve the accuracy of routine PL measurements of film composition.

Accomplishments:

Room temperature PL measurements were performed on several $Al_xGa_{1-x}As$ film / GaAs substrate samples grown in the Optoelectronics and Semiconductor Electronics Divisions, with compositions (determined independently by WDS and RHEED) between x=0 to x=0.31. Significant results are as follows.

The observed PL peak energy showed a large shift with excitation power, up to 0.04 eV at incident power levels to 0.4 W. This shift is explained by local heating of the sample, due to the small laser spot size and short penetration depth, which leads to a large value of the absorbed power per unit volume. The heating also resulted in a broadening of the PL linewidth, and a change in the slope of the high-energy exponential tail of the PL spectrum. The slope of the high-energy exponential can be used to estimate the temperature of the excited sample volume; by this method, the temperature was found to be above 400 K at 0.4 W incident power. This result shows that the excitation intensity must be limited to avoid a PL shift due to heating.

Further excitation intensity dependence measurements were done after the conventional, spherical focusing lens was replaced with a cylindrical lens that produces a line-like rather than point-like focused beam profile. The line profile better matches the aspect ratio of the spectrometer

entrance slit. It was found that the onset of the heating effect occurred at considerably higher excitation power with the cylindrical than with the spherical lens. Further measurements were thus conducted with the cylindrical optics.

Rather than defining an absolute photon energy to be the primary measured parameter, we chose to define the difference between two PL energies, from an alloy ($x>0$) film and from a pure GaAs ($x=0$) film, as the primary parameter. This procedure has the advantage that it makes the choice of PL "marker" energy, such as the peak, or lower or upper half-maximum point, less critical. Our measurements showed that the energy difference between a given alloy film and the $x=0$ film stays constant for different choices of "marker" energy. Another way to state the advantage of the differential method is that with this method one only needs to determine an energy which is at a fixed offset from the band gap, rather than the true band gap energy, in order to measure composition.

Twelve different published model equations for the dependence of the band gap on composition were converted to the differential form, $E_G(x)-E_G(x=0)$, and used to calculate the compositions of the films (x) from the measured PL energy differences. A large discrepancy was found among the published models; the calculated value of x changed by as much as 0.04 at $x=0.20$, for the same measured energy difference, depending on the choice of model. It is likely that the accuracy of most of the model equations is poor due to the fact that they are not based on accurate, direct composition measurements. However, the most recently published model, based on work by the National Research Council of Canada, gave compositions that were in reasonable agreement with the compositions determined independently from RHEED and WDS. The largest discrepancy between the composition from PL with the NRC model, and from the other methods, was $\Delta x=0.006$. This implies that that only a small correction to the NRC model will be needed to achieve the best fit to our results.

PROGRAM TITLE: Ceramic Thin Film Measurements and Standards

PROJECT TITLE: Compositional Metrology of Dielectric Thin Films

Principal Investigators: Debra L. Kaiser and Igor Levin

Technical Objectives:

The objective of this project is to develop and apply methodologies for accurate composition measurements of dielectric thin films for electronic applications.

Technical Description:

Dielectric thin films are widely used in a variety of electronic devices. This project has focused on $Ba_{1-x}Sr_xTiO_3$ (BST), a leading candidate material for use in next generation dynamic random access memories (DRAMs), CMOS transistors, and voltage tunable devices for microwave communications. For each of these devices, the key properties of the material are strongly dependent upon the composition. For example, the dielectric constant in BST-DRAM films decreases by about 50% when the cation mole fraction of Ti is increased from 51% to 53.5%. Accurate measurement of the composition is essential for optimizing the performance of the material and the deposition process.

The project was initiated this year and has two major activities. The first is a joint project with the Chemical Science and Technology Laboratory (CSTL: J. Small, J. Armstrong) to develop methodologies for measuring the composition of thin films (with thickness ultimately down to 1-5 nm) for gate dielectrics. Our primary contribution to this activity is the fabrication of BST films of precisely known composition for the measurement studies. Spin coating was selected as the fabrication technique for these studies; the composition of a BST film produced by spin coating should be identical to the precursor solution composition, which can be synthesized with high compositional accuracy. We are also measuring the thicknesses of the films and characterizing the surface morphology.

The second major activity involves nanocompositional mapping and structure analysis of BST-DRAM films with Ti contents in the range of 50.7% to 53.4%. These studies were conducted to investigate the basis for the strong dependence of the dielectric constant on Ti concentration in these films. The composition measurements were performed at the National Institutes of Health on a dedicated scanning transmission electron microscope equipped with a parallel electron energy loss spectrometer.

External Collaborations:

The films for the compositional mapping and structure analyses were obtained from Advanced Technology Materials, Inc. (G. Stauf, P.C. Van Buskirk, S. Bilodeau, R. Carl); this collaboration also involves the National Institutes of Health (R. Leapman) and Argonne National Laboratories

(S. Streiffer). The BST precursor solution for the film deposition experiments was obtained from Raytheon (H. Beratan).

Planned Outcomes:

This research will provide U.S. industry with state-of-the-art methodologies for measuring the composition of ultra-thin dielectric films and nanometer-sized regions of dielectric films. Such methodologies are essential for the development of BST thin film composition standards. In addition, the studies on the BST-DRAM films will provide a basic understanding of the effects of film composition and structure on dielectric properties.

Accomplishments:

A spin coating apparatus was set up for the deposition of $Ba_{0.7}Sr_{0.3}TiO_3$ (BST) thin films for the composition measurement studies. The aqueous-based precursor solution contained Ba, Sr and Ti lactates, and was highly stoichiometric (i.e., mole ratio (Ba+Sr)/Ti = 1.00 ± 0.01, Ba/Sr = 2.43 ± 0.05). BST films were deposited on 5 cm (2 in) (100)Si wafers by spin coating a solution composed of 1 part precursor, 1½ part acetic acid, and 1 part ethylene glycol methyl ether at 3400 rpm for 30 s. The spun-on film was dried via a four-step process at nominal temperatures of 90 °C, 195 °C, 430 °C and 580°C, and subsequently annealed at 700 °C in flowing oxygen for 1 h to crystallize the BST phase. X-ray diffraction measurements on the films showed that the presence of polycrystalline BST. Thickness profiles of selected films were measured by reflectance mode spectrophotometry (P. Schenck); the thickness values ranged from 70 nm to 120 nm. For each specimen, the thickness values measured across the full specimen radius agreed to within ± 4%, indicating good thickness uniformity. Scanning electron microscopy examination (M. Vaudin) of a representative film revealed that the surface was largely featureless, with some microcracking. Films have been given to CSTL for use as standards to modify the analytical correction procedures used in various microanalytical techniques for measuring composition, including multiple voltage electron microprobe analysis, electron energy loss spectroscopy, low voltage probe analysis, and Auger spectroscopy.

High-spatial resolution electron energy loss spectroscopy (EELS) and high resolution electron microscopy measurements were conducted on BST-DRAM films with Ti contents ranging from 50.7% to 53.4%. The films, obtained from Advanced Technology Materials Inc., were deposited on $Pt/SiO_2/Si$ substrates by metalorganic chemical vapor deposition. Maps of the Ti-$L_{2,3}$ and the Ba-$M_{4,5}$ absorption edge intensity distributions were obtained from the EELS spectra; these data were quantified using a $BaTiO_3$ single crystal standard. The measurements on each film showed that the grain boundaries had a higher Ti/Ba ratio than the grain interiors. In addition, films with greater than 52% Ti contained an amorphous Ti-rich phase at some of the grain boundaries and multiple grain junctions; the amount of this phase increased with increasing overall Ti content. Since the grain size was found to be independent of the average composition, the grain boundaries alone cannot account for the strong compositional dependence of the dielectric constant. The analyses further indicate that the amorphous phase can only partially account for the significant drop in the dielectric permittivity accompanying increases in the overall Ti/(Ba+Sr) ratio. Quantitative spectrum imaging studies suggest that, in films with overall Ti contents greater than

50%, the "excess" Ti is accommodated by the creation of Ba/Sr cation vacancies which segregate to the grain boundary regions. These nanocomposition and structure results are important for understanding the dielectric constant dependence on composition, and for optimizing the deposition process of BST-DRAM films.

Publications:

I. Levin, R.D. Leapman, D.L. Kaiser, P.C. Van Buskirk, S. Bilodeau, and R. Carl, "Accommodation of Excess Ti in a $(Ba,Sr)TiO_3$ Thin Film with 53.4% Ti Grown on $Pt/SiO_2/Si$ by Metalorganic Chemical Vapor Deposition," Appl. Phys. Lett., **75**, 1299 (1999).

PROGRAM TITLE: Ceramic Thin Film Measurements and Standards

PROJECT TITLE: Ferroelectric Poling and Domain Stability

Principal Investigators: John Blendell, Lawrence D. Rotter, Peter K. Schenck, Grady White

Technical Objective:

The objectives of this research project are to develop measurement techniques for evaluating ferroelectric domain structure, poling efficiency and domain stability, and to advance the basic scientific understanding of domain motion.

Technical Description:

Ferroelectric domains are clusters of unit cells in which the dipoles are aligned. Ferroelectric domain structure, or the arrangement of domains with different dipole orientations, dominates the properties of ferroelectric oxide thin films and their performance and reliability in integrated ferroelectric nonvolatile memory devices, microelectromechanical systems (MEMs), pyroelectric detectors, and optoelectronic devices. For example, in the case of the memory devices, the individual domains or groups of domains that comprise a single memory cell must switch orientations in a reproducible manner upon repeated read/erase/write operations and, in the absence of a switching field, must be stable over time. A piezoelectric atomic force microscopy (AFM) technique has been used to observe and to manipulate 180° domains in $Pb(Zr,Ti)O_3$ (PZT) thin films with the polar *c*-axis oriented out of the plane of the $Pt/SiO_2/Si$ substrate. In the measurements, an applied AC electric field (1 MV/m to 10 MV/m) causes changes in the dimension of the ferroelectric film due to piezoelectric behavior. Such changes have been observed by atomic force microscopy and the phase shift of the response is directly related to the orientation of the polarization of the sample. The response varies from in-phase response (when the polarization is in the direction of the applied field) to no response (when the polarization is in the plane of the film) to response which is 180° out of phase (when the polarization is in the opposite direction to the applied field). This year's activities have focused on observing the effect of applied field on domain stability, and on extending the technique to determine the crystallographic alignment of individual grains.

External Collaborations:

PZT films were obtained from Y.E. Lee of Seoul National University.

Planned Outcome:

This research should provide present and future U.S. industries engaged in ferroelectric oxide thin film device development with appropriate measurement tools to evaluate domain structure, polarization efficiency and domain stability in ferroelectric thin films. In addition, the research will provide a fundamental knowledge base on the microstructure/property relationships relevant to these domain issues.

Accomplishments:

The polarization direction in 100 nm regions of the PZT films was switched by applying a DC electric field of 10 MV/m to 100 MV/m through the AFM tip. It was observed that the polarization was not uniform over individual grains, indicating the presence of domains smaller than the grain size. It was also observed that the domains were not all switched by a large DC electric field (50 MV/m to 100 MV/m). Even in regions where the grains appeared uniformly aligned at low resolution (100nm/pixel), higher resolution (10nm/pixel) revealed that unaligned domains existed within the grains. When small regions (<1 μm) were switched with moderate electric fields (10 MV/m), there was a tendency for these regions to relax back to their original state. Larger regions, which were switched with higher fields (50 MV/m to 100 MV/m), were more stable. When large regions were aligned using the AFM it was possible to create small regions of opposite alignment within these large regions. Further work is in progress to quantify the dependence of domain stability on applied field.

It was also determined that the magnitude of the response, in addition to the phase of the response, yields information about the crystallographic alignment of the grains. While the phase of the response gives the direction of polarization (i.e. up, down, or in-plane), it does not give any information about the orientation of the polar axis relative to the film normal. By analyzing both the magnitude and phase of the response, it should be possible to determine the orientation of the polar axis. Initial results have shown that this is feasible. The system will be upgraded in the coming year to improve the resolution of these measurements.

A project to produce films of PZT by pulsed laser deposition (PLD) was initiated. Using the existing PLD facility and a commercial PZT target, amorphous films were deposited on Pt coated Si substrates, on MgO substrates and on indium-tin oxide (ITO) coated glass substrates. The films were crystallized in a lead-containing sarcophagus to prevent Pb loss. It was found that relatively high temperatures (700 °C) were required to crystallize the films and diffusion of material from the substrate into the film may be a problem. This project is in the initial stages; films produced by PLD will be examined by both optical techniques and AFM.

PROGRAM TITLE: Ceramic Thin Film Measurements and Standards

PROJECT TITLE: Optical Characterization Techniques

Principle Investigators: Lawrence H. Robins, Lawrence D. Rotter, Peter K. Schenck

Technical Objective:

The objective is to develop and use optical characterization techniques for the measurement of critical properties of thin film and multilayer structures of importance to the photonics and electronics industries, in particular structures in which the active layers are composed of group III nitride or ferroelectric oxide materials.

Technical Description:

Measurement techniques including cathodoluminescence (CL) imaging and spectroscopy, photoluminescence (PL) excitation and emission spectroscopy, Raman spectroscopy, transmittance and reflectance mode spectrophotometry, second harmonic generation, polarimetry, and prism coupling are used to determine thin film and substrate properties such as thickness, optical constants, electronic band gap, defect and impurity energy levels, structural and compositional phase content, residual stress/strain, electro-optic constants, waveguiding losses, internal electric fields, and ferroelectric poling efficiency. This year's activities have focused on: 1) the correlation of optical, structural and chemical measurements to provide information about compositional inhomogeneity of indium gallium nitride ($In_yGa_{1-y}N$) films for visible-emitting photonic devices; 2) a comparison of two methods for analyzing spectrophotometry data; and 3) the development of a spatially resolved reflectance mode spectrophotometry technique for measuring the thickness and optical properties of thin films.

External Collaborations:

Group III nitride samples were obtained from C.A. Parker, S.M. Bedair and coworkers at North Carolina State University (NCSU), J.H. Edgar at Kansas State University, S. Donovan and S.J. Pearton at the University of Florida, and J. Ari Tuchman at Principia Lightworks. Lead zirconate titanate (PZT) films for thickness measurements were obtained from G. Fox at Ramtron Corp.

Planned Outcomes:

This work will establish the composition dependencies of the band-edge luminescence peak width and the x-ray diffraction (XRD) θ-2θ peak width (an indirect measure of compositional inhomogeneity) in $In_yGa_{1-y}N$ films, and will ascertain if there is a correlation between the two different peak width measurements. Such a correlation would provide additional information about the relation between the atomic and electronic structure of the films. The variation of the optical properties of $In_yGa_{1-y}N$ and aluminum gallium nitride ($Al_xGa_{1-x}N$) films with composition, especially in the energy range above the band gap, will be determined by measuring films with different compositions but otherwise similar deposition parameters.

This work will demonstrate the utility of a rapid, simple, reflectance mode spectrophotometry technique for routine mapping of the thickness and optical properties of thin film materials with a spatial resolution of better than a millimeter.

Accomplishments:

A set of sixteen $In_yGa_{1-y}N$ films grown by metalorganic chemical vapor deposition on GaN buffer layers on sapphire (from C.A. Parker and S.M. Bedair, NCSU), with thicknesses from 0.4 μm to 1.0 μm and compositions from y=0.05 to y=0.47, were examined by several structural and optical characterization techniques. Pure GaN (from the NCSU group) and InN (from the University of Florida group) films were also examined. Key results of this work are as follows.

The In/(In+Ga) ratio (y) of each alloy film was determined accurately by wavelength dispersive x-ray spectrometry in an electron microprobe, with InAs and GaP standards (collaboration with John Armstrong, Surface and Microanalysis Science Division). Several spots were examined on each sample; the compositions were found to be highly uniform on a macroscopic (100 μm) length scale. The c lattice constants were measured by XRD θ-2θ scans in the vicinity of the low-angle 0002 and high-angle 0006 diffraction peaks. The lattice constants of the alloys and the endpoint compounds (GaN, InN) were found to vary linearly with In fraction to good accuracy; i.e. Vegard's Law is obeyed for this system. (Note the lattice mismatch between the endpoints is 10 %.) The 0006 XRD peak widths of the alloys generally increase with In fraction. According to a model calculation which converts the XRD peak width to an upper limit for the compositional inhomogeneity, the local In fraction varies by less than $\Delta y=0.05$ in films with average In fraction less than y=0.25. A small amount of nearly pure InN was detected by XRD only in the films with y>0.4, indicating true phase separation in these films.

The optical band gaps (absorption edges) of the pure and alloy films were determined by transmittance spectroscopy. The pure InN film was found to have a room temperature band gap of ~1.2 eV, and the absorption coefficient was found to increase above the bandgap with a power-law exponent of 1.75, i.e. as $(E-E_G)^{1.75}$, rather than an exponent of 0.5 as expected for a direct-gap semiconductor. One possible cause for this behavior is a large carrier concentration, which may produce a broad impurity band that merges with the conduction band (degenerate doping case). (The electrical properties of the film have not yet been measured.) The structure of the InN film was verified by XRD scans of the 0002, 0004, and 0006 diffraction peaks; the c lattice constant was found to be 0.5705 nm, the same as reported by several other researchers.

When the optical band gaps of all the samples, both pure and alloy films, are plotted as a function of composition (from WDS), the composition dependence is found to be accurately represented by a quadratic function. If we assume that our measured value of the band gap of InN is correct, the best-fit values of the coefficients of this function are:

$E_G(y)$ (electron-volt units) $= 3.37 - 2.20y - 3.28y(1-y)$
The third coefficient, 3.28 eV, gives the deviation of the composition dependence of the band gap from linearity and is called the bowing parameter. The large observed value of the bowing parameter may be an indication of compositional inhomogeneity in the alloy films.

Another component of this project is the development of improved measurement and data analysis methods that are broadly applicable to optical measurements of thin films. The scattering of electromagnetic waves from rough surfaces is a longstanding problem in electromagnetism and optics. For analyzing ellipsometry data the rough surface is typically modeled as an effective medium layer. For analyzing spectrophotometry data the Fresnel coefficients of the rough interfaces are typically modified by Debye-Waller type factors. The effective medium method is starting to be used for analyzing spectrophotometry data as well (it's available in commercial software packages). The two methods of analyzing spectrophotometry data were compared numerically, and it was shown that the effective medium method did not reproduce the effects most commonly seen with rough surfaces (i.e., effects other than the moth's eye effect, wherein the transmittance of a rough surface acts as an antireflection coating), whereas a large body of data (as well as an ASTM standard) supports the use of the other method. Work on combining the two methods when analyzing spectrophotometry data has begun.

A variation on reflectance mode spectrophotometry, utilizing a miniature fiber optic coupled spectrometer, has been developed for measuring the thickness and optical properties of thin films. The instrument uses a bifurcated fiber optic probe to illuminate the sample and record the reflectivity of the film-substrate relative to the bare substrate. The advantage over conventional reflectance mode spectrophotometry is that the whole spectrum is taken simultaneously and variations in the film can be quickly mapped out in two dimensions with a spatial resolution better than a millimeter. This instrument has been used to map out the thickness of NIST films produced by metalorganic chemical vapor deposition, spin coating, and pulsed laser deposition as well as sputter deposited films from industry.

To test the accuracy of the spatially resolved reflectance spectrophotometry measurements, x-ray reflectivity and ellipsometry were also used to determine the thickness of a sputter deposited PZT film from Ramtron. A Rudolf manual nulling ellipsometer was retrofitted with a HeNe source and photodiode detector. It was used to measure the optical constants of a Pt/Si substrate and the optical constants and thickness of a PZT/Pt/Si thin film, both from Ramtron. The PZT thickness determined by ellipsometry agreed with the thickness determined by x-ray reflectivity. It was found that the accuracy of the spatially resolved reflectance spectrophotometry measurements could be improved by using the ellipsometry results to modify the literature values of the optical constants of Pt.

Publications:

L.H. Robins, A.J. Paul, C.A. Parker, J.C. Roberts, S.M. Bedair, E.L.Piner, N.A. El-Masry, "Optical absorption, Raman, and photoluminescence excitation spectroscopy of inhomogeneous InGaN films," MRS Internet J. Nitride Semicond. Res. 4S1, G3.22 (1999)

J.H. Edgar, L.H. Robins, S.E. Coatney, L. Liu, J. Chaudhuri, K. Ignatiev and Z. Rek, "A Comparison of Aluminum Nitride Freely Nucleated and Seeded on 6H-Silicon Carbide," submitted to Proceedings of the International Conference on Silicon Carbide and Related Materials 1999 (ICSCRM'99)

C. A. Parker, J.C Roberts, and S.M. Bedair, M. J. Reed, S. X. Liu, N. A. El-Masry and L. H. Robins, "Optical Band Gap Dependence on Composition and Thickness of $In_xGa_{1-x}N$ ($0<x<0.25$) Grown on GaN," Appl. Phys. Lett., in press

L.D. Rotter, "A comparison of two computational methods for determining the surface roughness of transparent solid interfaces from spectrophotometric transmittance and reflectance data," submitted to Applied Optics.

PROGRAM TITLE: Ceramic Thin Film Measurements and Standards

PROJECT TITLE: Texture Measurements and Effects

Principal Investigators: Mark D. Vaudin and Peter K. Schenck

Technical Objectives:

The objective of this project is to develop fast, accurate x-ray diffraction (XRD) techniques for measuring crystalline texture in thin films and for quantifying the relative abundances of specific preferred grain orientations in a film.

Technical Description:

The crystallographic texture of thin films of technologically important materials frequently has a strong effect on the properties of these films. For example, the remanent polarization in ferroelectric films such as $Pb_xZr_{1-x}TiO_3$ (PZT) is texture-dependent, so the ability to switch domains in a PZT non-volatile memory device is strongly influenced by the texture. In the case of copper, which has anisotropic stiffness coefficients, texture can affect uniformity of a film during chemical mechanical polishing (CMP), a processing step used in advanced metallization of microcircuits. Polycrystalline films of many different materials often contain distinct populations of grains with different preferred orientations (e.g., a bimodal distribution of (100) and (110) oriented grains) and the relative volume fractions of the different orientations may depend upon the film deposition conditions. Thus, measuring the relative abundance of the different preferred orientations and relating this information to processing and properties can be crucial for optimizing a thin film material.

Over the past several years, we have developed techniques for measuring texture in thin film and bulk materials that use conventional powder diffractometers, equipment commonly available in industrial and university laboratories. Preferred crystallographic orientation is measured by recording two x-ray scans from the sample: 1) a conventional θ-2θ scan of a Bragg peak from the textured planes; and 2) an ω-scan (rocking curve) using this peak. The raw data are corrected for defocus to obtain accurate full-width-at-half-maximum and intensity values for the peak measurements. To determine the volume fractions of the differently textured grains, diffraction patterns are obtained from a randomly oriented powder specimen of the same material to relate the integrated intensities of different Bragg peaks.

This year's activities have focused on texture measurements of a variety of thin film materials, including $BaTiO_3$ and $(Ba,Sr)TiO_3$ films deposited in-house on Pt/Si substrates by pulsed laser deposition (PLD), PZT films from Ramtron Corporation deposited by sputtering on Pt/Si, and Cu films electrodeposited on Si-based substrates, both in-house and by Semitool Corporation. Another aspect of this project involves extending the ideas of defocus correction, which have been successfully applied to the powder diffractometer case, to 4-circle texture diffractometry where complete 3-D texture is obtained. The initial theoretical framework for the correction has been developed.

External Collaborations:

NIST is collaborating with G. Fox at Ramtron Corporation on experiments and theoretical formulations to determine the relative abundances of various textured populations in PZT films. For these studies, Ramtron has provided films with mixed (100), (111) and random texture distributions.

A collaboration on the application of defocus corrections to 4-circle texture measurements has been initiated with K. Rodbell and T. Shaw at IBM.

Planned Outcomes:

This research will provide U.S industry with fast, accurate x-ray diffraction (XRD) techniques for measuring crystalline texture in thin films and for quantifying the relative abundance of differently textured grain populations. The techniques will use a powder diffractometer and will therefore necessarily concentrate on the axisymmetric components of texture.

The techniques will be extended to 4-circle texture diffractometry measurements. New approaches to texture (and other x-ray) measurements will be explored utilizing the new high resolution x-ray diffraction facility to be completed in the coming year.

Accomplishments:

The software package for Windows 95 that was developed to perform the intensity correction calculations and provide the user with texture data in the form of corrected rocking curves can now be downloaded at http://www.ceramics.nist.gov/webbook/TexturePlus/texture.htm.

Texture measurements were conducted on $BaTiO_3$ and $(Ba,Sr)TiO_3$ thin films deposited by PLD under various conditions. For $BaTiO_3$, a series of films was deposited at various laser fluences on a number of substrates with different adhesion interlayers between the Si/SiO_2 underlayer and the (111)-textured Pt top layer. The lattice parameters of the $BaTiO_3$ layer were found to increase with fluence from the bulk value at 1 J/cm^2 (low fluence) to a value ~2% higher at 10 J/cm^2. The substrate type had no effect on the observed variation in lattice parameter with fluence. However, the textures of the $BaTiO_3$ films were affected by the nature of the interlayer; in agreement with previous findings, (110) oriented $BaTiO_3$ was favored by the presence of a Ti interlayer, but (100) $BaTiO_3$ was found to predominate when there was no Ti interlayer.

For $(Ba,Sr)TiO_3$, a series of films was deposited on (111) textured Pt/Si substrates at temperatures of 500 °C, 550 °C and 600 °C. At 500 °C, the film displayed a (100) oriented texture, and also an amorphous fraction, the amount of which decreased as the deposition temperature was raised. At 550 °C, the (100) fraction increased and a (110) texture developed. The (110) fraction became substantial at 600 °C, while the (100) fraction decreased.

In addition to texture characterization, microstructural characterization of the $BaTiO_3$ and $(Ba,Sr)TiO_3$ thin films by scanning electron microscopy, wavelength dispersive x-ray spectrometry, atomic force microscopy, and optical reflectometry methods is being carried out for correlation with the XRD measurements, so that mechanisms and driving forces for texture and microstructure development can be determined.

Publications:

Mark D. Vaudin, "Accurate Texture Measurements on Thin Films Using a Powder X-ray Diffractometer," (Proceedings of the 12th ICOTOM conference).

Yong Eui Lee, Mark D. Vaudin, Peter K. Schenck, and Bernard Hockey, "Micro-texture of $BaTiO_3$ thin film fabricated by pulsed laser deposition on $Pt/Ti/SiO_2/Si$ substrate," submitted to Journal of Materials Research.

PROGRAM TITLE: Ceramic Thin Film Measurements and Standards

PROJECT TITLE: Thermal Measurement Development

Principle Investigators: Albert Feldman, Eduardo J. Gonzalez, Daniel Josell (855), and Grady S. White

Technical Objective:

The purpose of this research project is to develop new methods, evaluate the accuracy, and exploit the capabilities of different thermal diffusivity or thermal conductivity measurement techniques used for the study of bulk specimens and thin films. Our objective is also to develop and modify measurement methods so that accurate determinations of anisotropic thermal transport and interface boundary thermal resistance can be made.

Technical Description:

The need for measurement techniques that address issues such as interface thermal resistance, thermal conductivity dependence on film thickness, and non-isotropic heat flow was noted in a conference report describing the Workshop on Thin Film Thermal Conductivity Measurement held at the Thirteenth Symposium on Thermophysical Properties in Boulder, CO, June, 1997. To address these issues, an interdivision round robin of thermal diffusivity and conductivity measurements between the Ceramics, Metallurgy, and Polymers Division was conducted to study the sensitivity, accuracy, and limitations of three different measurement techniques; the Mirage method, the thermal pulse method, and the 3-omega method. A set of test samples was selected that incorporated specimens with low thermal conductivity, e.g., films of polyimide on Si and GaAs, films of polystyrene on Si, and specimens with high thermal conductivity, e.g., AlN. By comparing the test results obtained with the different techniques, we have attempted to identify the limitations and uncertainties of each method. Furthermore, we identified ways to improve the methodologies.

An international round robin for thin film thermal conductivity measurements has also been organized under the auspices of the Versailles Project on Advanced Materials and Standards (VAMAS) with the objective of developing a consensus on measurement methods for thermal properties of thin films. The specimens selected for this round robin consisted of silicon wafers that had been oxidized to produce amorphous silicon dioxide films having nominal thicknesses of 500 nm, 200 nm, 100 nm, or 50 nm. Separate specimen sets had been sent to 18 laboratories in the U.S., Korea, Japan, China, and Germany. The results from this round robin will be presented in the Workshop on Thin Film Thermal Conductivity Measurement to be held at the Fourteenth Symposium on Thermophysical Properties in Boulder, CO, June, 2000.

In addition to the ongoing round robin activities, we have applied a novel analysis method to Mirage data for the purpose of evaluating thermal diffusivity anisotropy, interface thermal resistance, and other microstructural features such as porosity. We have measured anisotropic heat flow in Al/Ti multilayer thin films by calculating the in-plane and out of plane diffusivity.

Multilayers of Al/Ti were deposited on Si substrates by e-beam evaporation; the thicknesses of the individual layers were systematically varied from 2.5 nm to 40 nm, to a total nominal thickness of 3 μm. The dependence of the in-plane and normal diffusivities on the bilayer thickness was also used to determine an interface thermal resistance. For comparison, measurements were also made on Cu films varying in thickness from 0.5 μm to 5 μm. Finally, we have extended our investigation of anisotropic heat flow to polymer films, such as polyimide and polystyrene.

External Collaborations:

The Ceramics Division is leading an interdivision thermal conductivity and thermal diffusivity round robin effort that includes three different measurement techniques within the Ceramics, Metallurgy, and Polymers Division.

The Ceramics Division is also leading an international thermal conductivity round robin under the auspices of the Versailles Project on Advanced Materials and Standards (VAMAS). Eighteen laboratories from five countries had agreed to participate.

We are collaborating with Intel by performing thermal measurements on polymer films and insulating tapes used in the packaging of microprocessors. Furthermore, we are assisting Intel in developing measurement techniques that they can perform in-house.

We are collaborating with the University of Alberta, Canada, in a study of porous ZrO_2 films which have possible novel thermal insulating properties. We are collaborating with North Carolina State University to study high conductivity films of AlN.

Planned Outcomes:

Results from both the interdivision and VAMAS activities are expected to allow for a critical assessment of different techniques that are used to measure the thermal conductivity of thin films. Thus, we may gain an understanding of the physical limitations and sensitivity of each technique.

Our continuing research work on thin films has provided critical data on interface thermal resistance and heat flow anisotropy. We are currently attempting to manipulate the microstructure at the interfaces of aluminum/titanium multilayers in order to control the magnitude of the interface thermal resistance.

Accomplishments:

Interdivision Round Robin: The results from the round robin indicate that the 3-omega and the thermal pulse are very good methods for measuring the diffusivity of low thermal conductivity films such as polyimide and polystyrene. The Mirage method appears to have difficulties with low thermal conductivity materials (see Table 1). We believe that this may be a result of an error in the original formulation of the modeling equations that underestimates the impact of the air above the specimen. For systems where the $\kappa_{air} << \kappa_{film}$, the effect of this error is very small as described in an earlier publication. However, this effect can be significant when κ_{film} is closer in magnitude

to κ_{air}. We are presently correcting the data analysis computer code for these errors following the newly derived equations. We will analyze the Mirage data again with the corrected formulation of the theory.

Table I. Thermal Diffusivity and Estimated Standards Uncertainty Measured with Three Different Methods

	Diffusivity ($cm^2 \cdot s^{-1}$)		
	Thermal		
Method Used:	**Mirage**	**3-omega**	**Thermal Pulse**
Polyimide on Si	α^p = 0.0163 ± 0.0018 α^n = 0.0031 ± 0.0001	0.00106 ± 6 x10^{-5}	0.00108 ± 8 x10^{-9}
Polyimide on GaAs	α^p = 0.0131 ± 0.0029 α^n = 0.0016 ± 0.0001	0.00106 ± 4.2 x10^{-6}	-
Polystyrene on Si	α^p = 0.0003 ± 5 x10^{-5} α^n = 0.0002 ± 3 x10^{-5}	0.0006 ± 3.0 x10^{-5}	0.0006

(α^p stands for in-plane thermal diffusivity and α^n for normal diffusivity)

VAMAS Thermal Conductivity Round Robin: The round robin has been completed and the data are being analyzed.

Thermal Transport Properties of Multilayer Thin Films: The thermal diffusivity of multilayer films, both normal and parallel to the layers, has been measured with the Mirage method. The thermal diffusivities of the multilayer films were substantially less than the thermal diffusivity predicted on the basis of bulk material values for each of the constituent materials, both in the plane of the layers and normal to the layers. This effect has been attributed to interface boundary thermal resistance for heat flow normal to the interfaces and a combination of interface and grain boundary resistance for in-plane heat flow. The dependence of the in-plane and normal diffusivities on the bilayer thickness was used to determine an interface resistance of 1.6 x 10^{-6} $cm^2 \cdot K \cdot W^{-1}$. For comparison and calibration purposes, Cu films were also tested. The Cu films were found to possess essentially isotropic thermal diffusivities that were within 10% of bulk values; in the thicker films, annealing reduced this difference to about 5%.

Modeling: We have extended the use of the three omega technique to systems with substrates of finite thickness and to multilayer systems with any number of layers. This has allowed us to obtain interface thermal resistance in the case of a CVD diamond specimen. It also has allowed us to model the three omega signal due to a thermal conductivity profile that varies in a direction normal to the top surface of the specimen.

Publications\Communications:

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E. J. Gonzalez, D. Josell, J. E. Bonevich and G. White, "Thermal transport through thin films: Mirage technique measurements on aluminum/titanium multilayers", Submitted to the Journal of Materials Research.

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J.H. Kim, A. Feldman, and Donald Novotny, "Application of the three omega thermal conductivity method to a film on a substrate of finite thickness", Journal of Applied Physics 86, 3959-3963 (1999).

PROGRAM TITLE: Ceramic Thin Film Measurements and Standards

PROJECT TITLE: X-ray Procedures

Principal Investigators: Charles E. Bouldin, James Cline, Bruce D. Ravel, Mark D. Vaudin, Nicholas Armstrong, Gery Stafford (855), Debra L. Kaiser

Technical Objective:

The broad objective of this project is to develop and utilize advanced x-ray characterization methods for thin film materials used in electronic and photonic applications.

Technical Description:

Most technologically important electronic and photonic materials are prepared as thin films on a variety of substrates. The properties of such films are dependent upon the phase composition, stoichiometry, texture of the phases, strain, and film thickness. We are developing and utilizing a variety of x-ray methods to characterize these features of films, including x-ray absorption and resonant x-ray diffraction using synchrotron radiation (National Synchrotron Light Source, Brookhaven National Laboratory), and x-ray reflectivity and diffraction using conventional laboratory x-ray sources and rotating anode sources. This year's specific activities have included: 1) identification of the phase composition of $(Ba,Sr)_yTiO_{2+y}$ (BST) thin films of varying chemical composition; 2) determination of local mixing of Ga and In atoms in $In_xGa_{1-x}N$ thin films; 3) measurement of BST and low-k dielectric film thickness; 4) development of an improved methodology for measuring thermal expansion coefficients in low-k dielectric films; 5) measurement of grain growth during recrystallization of electrodeposited Cu films; and 6) development of a state-of-the-art, high-resolution thin film diffractometer.

External Collaborations:

Extended x-ray absorption fine structure (EXAFS) spectroscopy has been applied to several thin film systems to determine variations in structure and composition. This work has been done in collaboration with Micron, Texas Instruments, Allied Signal, Advanced Technology Materials, Inc., North Carolina State University, Argonne National Laboratory, Samsung Electronics, City University of New York, University of Washington, University of Florida and Johns Hopkins University. X-ray reflectivity has been used to measure thicknesses of BST films obtained from IBM and Texas Instruments, and to determine the thermal expansion coefficients of low-k dielectric films obtained from Allied Signal.

Planned Outcomes:

This research will provide U.S. industry with advanced x-ray characterization methods for evaluating thin film materials. Further, the synchrotron x-ray studies will provide insight into the local structural variations in films due to small changes in film composition that may be correlated with changes in properties; for example, measurements on BST films will provide structural

information that is critical in understanding the dielectric response of these films. The development of techniques to measure film thickness, thermal expansion coefficient and interface roughness by x-ray reflectivity, and texture, grain size and microstrain by x-ray diffraction would have broad-based applicability to U.S. industries producing thin film devices.

Accomplishments:

EXAFS measurements were conducted on a series of $(Ba_{0.94}Sr_{0.06})_yTiO_{2+y}$ thin films (y = 0.32 to 1.65) deposited on MgO substrates by metalorganic chemical vapor deposition. This composition series includes films that are close to the ideal BST stoichiometry (y = 1), as well as films that are far removed from ideal stoichiometry. Ab-initio calculations and EXAFS results on the films and on known standards such as bulk BST were used to identify the phase composition of the off-stoichiometry samples. Both the calculations and the measurement of known standards show that the off-stoichiometry films contain material that is amorphous; the stoichiometry variation is accommodated by the inclusion of Ti in oxygen coordination that is 4, 5 and 6-fold. Films with y > 1 contain amorphous Ba_2TiO_4. Across the rest of the composition range ($0.32 < y < 1.02$), there is a gradual variation in the amount of 4, 5 and 6-fold oxygen coordination. Similar results have been observed in EXAFS studies of Ti-oxygen mineral structures, and in radiation-damaged (metamict) Ti-O mineral systems. It is likely that the low deposition temperature used in the BST film deposition process resulted in amorphous Ti-O structures with disorder similar to that of radiation damaged material. Similar analysis of EXAFS data on $Ba_{0.7}Sr_{0.3}TiO_3$ films with cation mols fraction of Ti from 51% to 53.5% is in progress to elucidate the structural origin of the dielectric constant dependence on Ti content in these films.

The short range atomic structure of a series of $In_xGa_{1-x}N$ films was probed by EXAFS using grazing incidence excitation and In K-edge fluorescence detection. The results indicate that the mixing of Ga and In atoms is close to the average value determined by wavelength dispersive x-ray spectrometry. Since the short range order (on a 3 Å length scale) closely tracks the long range order, the EXAFS results appear to rule out the "InN" quantum dot model for the structure of $In_xGa_{1-x}N$ which has been proposed by other researchers. Optical measurements on these films are described in the "Optical Characterization Techniques" project summary in this report.

X-ray reflectivity measurements of film thickness have been made on a series of BST films on $Pt/SiO_2/Si$ substrates from IBM and Samsung Electronics. Results indicate that it is possible to determine thickness with a relative standard uncertainty of 0.5%, i.e., 0.15 nm uncertainty in a 30 nm thick film. These results also suggest that, with further analysis, it may be possible to determine the roughnesses of the surface and buried interfaces from the reflectivity data.

X-ray reflectivity measurements have been made to accurately determine the thickness and thermal expansion coefficients of low-k dielectric films on silicon substrates. These dielectric films are used to separate the vertically stacked conductive layers in high density integrated circuits. The thermal expansion mismatch between the dielectric and active layers results in cracking, a leading cause of chip failures. We have developed an improved methodology for determining layer thickness from x-ray reflectivity data that utilizes Fourier analysis. Thermal expansion coefficients are then calculated directly from thickness values measured at different

temperatures. Thermal expansion coefficients of about 55 x 10^{-6} K^{-1} with an uncertainty of 55 x 10^{-6} K^{-1} can be measured with the improved analysis technique.

X-ray diffraction Bragg peak profile analysis has been used to measure grain growth during recrystallization of Cu films. Such films are being used for device connections on the latest generation of computer microchips. The films undergo spontaneous recrystallization at room temperature, a phenomenon which must be understood to allow for optimal implementation of this technology. X-ray measurements were performed on blanket Cu films electrodeposited on Si-based substrates using different bath chemistries. Initial results show that the grain size is initially below 0.1 μm and grows by up to an order of magnitude, accompanied by a reduction in the dislocation density from initially high levels. Further studies to determine the effect of the electrolyte bath composition on the kinetics of grain growth will be conducted on the new thin film diffractometer described below.

An x-ray diffraction technique developed at NIST to measure texture in thin film materials using conventional x-ray diffraction equipment has been used to study a number of technologically important thin film materials. This project entitled "Texture Measurements and Effects" is discussed in a separate section of this report.

A laboratory X-ray diffractometer which features multiple and easily interchanged optical configurations as well as state-of the-art components throughout is nearing completion. Three optical configurations are to be available: 1) High resolution parallel beam for analysis of thin films, utilizing channel cut elements in a Bartels type monochromator which can be set up in 2, 4 or 8 bounce configurations. A channel cut element is used for diffracted beam analysis. This configuration can also include a graded, parabolic multilayer as a pre-optic for a ~15 fold increase in intensity. 2) "Low" resolution parallel beam for analysis of powders, utilizing a dual multilayer optic which consists of a graded, parabolic multilayer element followed by a flat multilayer optic. The second element serves to improve the spectral and angular character of the incident beam. 3) A divergent beam optic for analysis of powders, utilizing a Johansson Ge monochromator crystal. The machine also features sub-arcsecond encoding on the theta and two-theta axes, a Kappa goniometer which provides phi and chi sample rotation axes, and a rotating anode X-ray source. The instrument will provide the following capabilities: first principles d-spacing measurements on both powders and thin films which are traceable to the SI; macro-strain measurements; micro-strain and particle size/shape determinations; full texture and epitaxy determinations; and x-ray reflectometry. Furthermore the instrument's modular design allows for flexibility with regard to future expansion in capabilities. The instrument, scheduled to be operational in spring 2000, will be used for a variety of film measurements, including the texture and x-ray reflectivity studies discussed here, as well as for the "X-ray Standards" project discussed in a separate section of this report.

Publications:

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D.L. Kaiser, M.D. Vaudin, L.D. Rotter, J.E. Bonevich, I. Levin, J.T. Armstrong, A.L. Roytburd, and D.G. Schlom, "Effect of Film Composition on the Orientation of (Ba,Sr)TiO_3 Grains in Ba,Sr)$_y TiO_{2+y}$ Thin Films," J. Mater. Res. **14**, 1 (1999).

DENTAL AND MEDICAL MATERIALS

The Dental and Medical Materials Program provides basic materials science, engineering, test methods, and standards to sectors of the health care industry for the development of new or improved materials and delivery systems. This program focuses on (1) development of improved dental restorative materials with greater durability, wear resistance and clinical acceptability; (2) development of improved bone fixation materials and (3) evaluation of biomaterials.

Dental restorative composites are heterogeneous materials having three essential phases: (1) a polymeric matrix which comprises the continuous phase, (2) fillers of various types, sizes, shapes and morphologies which constitute the disperse phase and (3) an interfacial phase that, in varying degree, bonds the continuous and disperse phases into a unitary material rather than a simple admixture. While all three phases are important in determining the properties of the composites, this program is focused primarily on the interfacial and polymer matrix phases. Since the polymerization shrinkage that occurs in the matrix phase is one of the most commonly cited deficiencies of dental restorative composites, resources are allocated to develop high conversion, durable, low shrinkage polymeric materials for use in dental resin and composite applications. The polymeric matrix of a dental composite typically is formed by free radical polymerization of a resin which is one or more vinyl monomers, usually of the methacrylate class. Polymerization is started either by the formation of initiating radicals from chemical reduction-oxidation (redox) reactions or by photochemical redox reactions.

Although only a minor component of these composites, the interfacial phase that develops from the interaction of the silane coupling agent with the polymer matrix and the siliceous filler exerts a profound effect on the properties of the composites. Because these composites are used in an aggressive, aqueous environment that constantly challenges the vulnerable silane mediated polymer-filler bond, understanding of this critical interfacial phase is being acquired so that strategies can be developed for its improvement.

The occupational and environmental hazards associated with the use of mercury-containing dental alloys are a recurring source of public concern. Since dental amalgams have performed exceedingly well over more than one hundred years, the development of a direct filling material still based on the common constituents of dental amalgams, other than mercury, is desirable. This project is focused on acid-assisted consolidation of chemically precipitated silver powders and property measurements of hand consolidated test compacts prepared with the tools and procedures normally employed by dentists. The observed values of flexural strength for the silver compacts were equal or superior to mercury amalgams. Corrosion resistance, microleakage and marginal toughness values of the compacts were found to be superior to those of amalgams. Wear and biocompatibility studies on the hand consolidated compacts are in progress.

Besides the dental materials projects, efforts are directed toward the development of improved bone fixation materials and the evaluation of biomaterials. A project, carried out in collaboration with the American Dental Association and the National Institute of Dental and Craniofacial Research, is directed at enhancing the biocompatibility and mechanical properties of composite

bone cements. The biomaterials evaluation effort centers on the NIST Orthopedic Wear Consortium which consists of four companies to develop accelerated wear test procedures for rapid screening of materials used in hip and knee replacements. This will accelerate the introduction of new biomaterials into practice.

Dental and medical research directions in support of the goals are established in collaboration with the American Dental Association (ADA), the National Institute of Dental and Craniofacial Research, the National Heart, Lung and Blood Institute, the US Food and Drug Administration, and guest scientists from the U.S. Navy and the U.S. Public Health Service. NIST has hosted research associates from ADA since 1928. Currently, the ADA Health Foundation sponsors 30 research associates at NIST. The collaborative relationship between that professional association and the federal government is unique, and continues to develop and transfer important new technologies to dentistry and medicine.

PROGRAM TITLE: Dental and Medical Materials

PROJECT TITLE: Wear Mechanisms of Biomaterials in Orthopaedic joints

Principal Investigator: Stephen M. Hsu

Technical Objectives:

This project aims to understand the basic wear mechanisms of ultra-high molecular weight polyethylene as influenced by load, cross-shear motions, and the degree of cross-linking. From this understanding, provide a scientific basis to relate accelerated testing methodology to long term simulator testing. This research is conducted in conjunction with an industrial consortium. The consortium was formed in Oct. 1996, by six Orthopaedic companies for a duration of two years. The consortium was renewed in 1999, for another two years.

Technical Description:

The approval process of materials used in human joints is expensive and time-consuming. As more and more new materials become available, a rapid screening methodology is needed to shorten the product development cycle, improve product reliability, and develop more durable components for the total joint replacements. The orthopedic consortium members supply hip and knee joint replacement parts worldwide. The current materials of choice are ultra-high molecular weight polyethylene (UHMWPE) and cobalt-chromium alloy. A new wear tester capable of cross-shear and computer controlled program-loading was designed and built. A seven day test method based on this tester was developed and this method was able to discriminate among three known materials. The consortium was renewed in 1999 to provide a scientific basis to validate the accelerated test methodology in the context of long term testing.

Collaborations:

This is a joint project between the Polymers Division and the Ceramics Division. Dr. John Tesk serves as the project manager providing liaison between NIST and the consortium members as well as participating in the technical effort. Dr. Dan Fischer of the Materials Microstructural Characterization Group in the Ceramics Division and Dr. S. Sambasivan (NSLS) participated in the analysis using Synchrotron Radiation X-ray absorption techniques. The consortium members provide guidance, materials, and data to the project as well as support for a postdoctoral fellow from the University of Maryland to work on the project. Prof. Aris Christou from the University of Maryland also provides support and guidance to the project.

Planned Outcomes:

The anticipated outcomes are: 1) understanding of the basic wear mechanism of ultra-high molecular weight polyethylene as a function of load, spike load, spike load period; 2) validation of the accelerated test methodology as compared to the wear mechanisms of long-term testing.

Accomplishments:

A novel wear tester was successfully designed and built. The tester has cross-shear motion provided by two independent motor-driven stages containing the test specimens. By varying the frequency and stroke length of the two stages, a wide variety of cross-shear patterns can be generated. A computer controlled spike loading capability was implemented. Based on this available tester, a short-duration test method was developed that mimics the loading history of human joints. Results on three UHMWPE materials with known wear levels supplied by the Orthopaedic Consortium suggest that correct ranking of materials was achieved using a test method with a seven day duration. As a result of this development, the consortium agreed to continue the collaboration for another two years to provide a scientific mechanistic understanding of short term testing so that long-term performance can be effectively assessed.

The effect of load on wear was evaluated. In the test method developed, as well as for orthopaedic testing in general, the load is not constant but simulates the walking gait load curve. So the load effect was checked by integrating the actual load curve per unit cycle over the test duration. The Labview program was modified to allow storing and integrating the actual load curve over time. This was compared to projection based on a typical load curve. A 5% consistently lower load was observed. This discrepancy was due to a periodic need to adjust for dimensional loss due to creep and wear. When wear was plotted against this actual sum of load curves, the separation between good and bad materials increases.

The molecular orientation of UHMWPE used in biological implants was analyzed at the National Synchrotron Light Source (NSLS) at Brookhaven National Laboratory as part of this project. That research is described in the Synchrotron Radiation section of this report.

Impacts:

Biomaterials is a rapidly growing business. The rapid development of new materials offers a great opportunity for technological advances in this important area. The cost of qualifying a biomaterial in the U.S. is high as well as time consuming. A rapid, effective screening test method will reduce costs, cut the lead time, and help to maintain the competitive edge of the U.S. biomaterials industry.

Publications:

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M. C. Shen, S. M. Hsu, J. A. Tesk, A. Christou, "Wear Analysis of UHMWPE using a Load Sum Method," submitted to the Biomaterials Society.

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MAGNETIC MATERIALS

Magnetic materials are pervasive throughout our society. They are used, for instance, in magnetic recording media and devices, in all motors, in all transformers, on credit cards, as permanent magnets, as magnetic sensors, on checks, in theft control devices, in automotive and small engine timing devices, in xerographic copiers, in magnetic resonance imaging (MRI) machines, in microwave communications, in magnetic separation, and in magnetic cooling. Magnetic materials include metals, ceramics and polymers at different size scales ranging from large castings to particulates, thin films, multilayers and nanocomposites.

In the present trend to make devices smaller, thereby reducing weight or increasing storage density, new magnetic materials are constantly being developed. One critical need for implementation of these materials is the development of the measurement science needed for their characterization, in terms of both material properties and performance. This is the focus of the Magnetic Materials Program. Proper measurements of key magnetic properties, determination of the fundamental science behind the magnetic behavior of these new materials, analyses of the durability and performance of magnetic devices and development of Standard Reference Materials are key elements of this program. Some information is only obtainable by the use of unique measurement tools at NIST like the neutron diffraction facilities at NCNR, or the magneto-optic indicator film apparatus for observation of magnetic domain motion. Of particular interest is understanding the magnetic behavior of low dimensional systems, in which one or more characteristic dimensions have been reduced to nanometer sizes. For these new materials, however, it is not known whether their exciting novel behavior is due to new physics or to a logical extension of large-size behavior to small dimensions. Consequently, implementation of this new type of material into marketable products is significantly delayed. NIST is providing the measurement science to address this critical unknown.

Areas of present study include the following:

- preparation and measurement of "spintronic" systems wherein spin dependent magnetic devices are integrated directly onto semiconductor chips
- processing of magnetic multilayers for optimal giant magnetoresistance effect
- observation and micromagnetic modeling of magnetic domains for understanding magnetization statics and dynamics in advanced and conventional materials
- measurement and characterization of nanoscale magnetic interactions in multilayers, nanocomposites, and low-dimensional systems, needed for understanding and applying the physics of these materials
- measurement and modeling of the enhanced magnetocaloric effect in nanocomposites
- structure and magnetic characterization of new superconducting materials

- nanotribology of magnetic hard disks, measurement of stiction, friction, and wear at the nanometer scale

- measurement and understanding the origin of magnetic exchange bias in conventional and advanced magnetic structures and devices

- development of magnetic sensors of mechanical properties for incorporation as *in situ* controls in a steel mill

- development of a measurement system for the preparation of an absolute magnetic moment standard

- preparation of magnetic measurement standards

By experimentally addressing important issues in magnetism, by bringing together the industrial and scientific communities through the organization of workshops and conferences in the area, and by the development and preparation of appropriate standards, NIST acts to accelerate the utilization of advanced magnetic materials by the industrial sector, and to enable industry to take advantage of new discoveries and innovations. In addition, close linkage with the national storage industry consortium (NSIC) which consists of 38 companies and a score of universities allows industrial relevance and partnership. Additional collaborations with Xerox, General Motors, Hewlett Packard, IBM, Seagate, and Motorola Corporations, for example, enable NIST to leverage its activities with the much larger, but complementary, capabilities of other organizations.

PROGRAM TITLE: Magnetic Materials

PROJECT TITLE: Nano-Tribology

Principal Investigators: Stephen M. Hsu, Richard S. Gates, Patricia A. McGuiggan, and Daniel A. Fischer

Technical Objectives:

The project focuses on the measurements of friction, wear, and durability of magnetic hard disk systems and the measurement of the nanomechanical and tribological properties of the ultra-thin lubricating film on the disks. Measurement and characterization of such thin films will enable the development of future ultra-high density data storage technology.

Technical Description:

The development of ultra-high density magnetic hard disk technology requires nanometer scale measurements of friction, wear, and durability between the head and the disk. Current technology with areal density of 0.31 Gbit/cm^2 (2 Gbit/in^2) uses an air bearing design flying at 20 nm distance above the disk. At 6.2 Gbit/cm^2 (40 Gbit/in^2) areal density the head needs to fly at 5 nm height above the disk. Computational models suggest that density of 15.5 Gbit/cm^2 (100 Gbit/in^2) or higher will be possible if some of the materials issues and tribological issues can be successfully resolved. Sufficient protection of the disk surface against wear as offered by the carbon overcoat and the lubricant layer (1 nm thick) is the critical technological barrier as the distance between the head and disk becomes smaller.

Working in conjunction with the National Storage Industry Consortium (NSIC) Tribology Working Group, we are developing new and novel concepts in protecting the magnetic hard disk surface *via* organized molecular film structures. Various monomolecular films are deposited on ultra-smooth disks over different carbon overcoat materials. Some of the disks are evaluated by industrial collaborators using standardized testing such as Constant Start & Stop (CSS) tests. Some of the disks are evaluated using the facilities at NIST which include specialized accelerated testing and surface film characterization using synchrotron x-ray facilities at the National Synchrotron Light Source. An ultra-soft X-ray Near Edge absorption spectroscopy technique has been developed to measure molecular orientation, film thickness, and surface bonds. Fundamental measurements of surface forces, film strength, and nano-mechanical properties are also being conducted to support the technological development effort by U.S. industries.

Collaborations:

Part of the project is supported by the intramural funding from the NIST Advanced Technology Program (ATP) in support of NSIC projects. NSIC consists of over 30 companies and some 25 Universities. We work closely with the Tribology Working Group, which consists of IBM, Readrite, Seagate, University of California at Berkeley, University of California at San Diego, Northwestern University, and Carnegie Mellon University.

Planned Outcomes:

In conjunction with NSIC, this project will; (1) develop laboratory test procedures to evaluate the wear and lubrication characteristics of magnetic hard disk systems, (2) establish a model of how monomolecular films interact and protect the magnetic disks, and (3) determine relationships between thin film structures and their nano-mechanical properties.

Accomplishments:

Various organic monolayers and monomolecular films were designed and deposited on the magnetic hard disks (CH_x and CN_x coated surfaces). The coated disks were evaluated for friction and durability in studies by the University of California at Berkeley using Constant Start and Stop tests (CSS) and at NIST, using the high speed spin stand inclined plane tests.

Dr. Simone Anders at Lawrence Berkeley Laboratory studied one of our samples using a micro-focused X-ray absorption spectroscopy and found chemical evidence of oxidation and oxidation products in the wear track on the hard disks. This was not expected nor postulated for a monolayer of perfluoroalkyl ether film. Previously published results all centered around physical processes such as molecular shear, thermal decomposition, tribochemistry, and catalytic decomposition by Lewis acid sites on the alumina surface (head material). An extensive search of antioxidants soluble in perfluoroalkyl ethers through contacts in the scientific community yielded several compounds from the Wright Patterson Air Force Base. Disks were coated with Z-Dol plus antioxidants and sent to Berkeley for testing. Results showed definite improvement in durability as well as substantial reduction in oxidation. A follow-up study on concentration effects and a basic research study on monolayer mixability and solubility have enabled the beginning of phenomonological understanding. Research at the National Synchrotron Light Source (NSLS) at Brookhaven National Laboratory has addressed the character of the interface of the Z-DOL hard coat and the magnetic media hard disk. This research is described in the Synchrotron Radiation section of this report.

We have also been working with one of our industrial collaborators to study the feasibility of vapor phase deposition of perfluoroalkyl ethers on hard disks. This would eliminate the need to break the vacuum and remove the disks outside to dip coat the lubricant onto the disks. Direct deposition of perfluoroalkyl ether reduce the possibility of air oxidation and contamination of the hard disk surfaces and reduce costs. A vapor phase deposition apparatus was designed and built in 1999. Kinetic data on rate of deposition as a function of molecular weight were collected. Samples from our industrial collaborator were also received and analyzed at Brookhaven Synchrotron Light Source using soft X-ray absorption spectroscopy. Samples coated with lubricant in vacuum right after the carbon deposition showed much stronger bonding strength than samples exposed to air.

A CRADA with Pennzoil was signed in July, 1999. NIST and Pennzoil will work on the use of cyclopentanes and their derivatives as potential candidates for hard disk lubrication. Initial test results showed the cyclopentanes were equivalent to Zdol in terms of frictional characteristics and volatility. Being a hydrocarbon base, there was no solubility problem as with fluorocarbons.

The potential of adding other functionalized molecules to form tailored films could open a new line of investigation in hard disk lubrication research.

Carbon overcoats are used on the magnetic hard disk surface to minimize friction and wear of the magnetic surface. The friction of amorphous carbon surfaces was measured in the Surface Forces Apparatus. This apparatus can not only measure the friction and applied load, but the microscopic area of contact as well. The result show that friction of the amorphous surfaces is adhesion controlled (dependent upon the area of contact). The friction was also found to decrease with increasing humidity.

Publications:

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MECHANICAL PROPERTIES OF BRITTLE MATERIALS

Mechanical properties are the source of the greatest benefits as well as the most severe limitations of ceramic materials. Owing to their high strength-to-weight ratio, their relatively inert behavior in aggressive environments, their high hardness and wear resistance, and their ability to withstand significantly higher temperatures than metals or polymers, ceramic materials offer the potential for major improvements in component design for a wide range of applications. On the debit side, however, ceramics typically exhibit statistically variable brittle fracture, environmentally enhanced subcritical crack growth, sensitivity to machining damage, and creep-deformation behavior at elevated temperatures. Additionally, a lack of techniques for detecting and quantifying critical flaws before failure ensues severely curtails current uses of ceramics. Unpredictable failure behavior of ceramics stems from three sources: (1) limited data and a deficiency of basic understanding of failure processes in ceramics; (2) limited standard test techniques to permit inter-laboratory comparisons of materials behavior and collection of engineering data; and (3) inadequate models and statistical techniques for life prediction and reliability analyses. The Mechanical Properties of Brittle Materials Program has components specifically addressing each of these issues.

Basic understanding of mechanical behavior of ceramics is investigated both at room temperature and at elevated temperatures. At room temperature, mechanical properties and failure processes are investigated in polycrystalline ceramics, glasses, and ceramic matrix composites as a function of microstructure, environment, and processing conditions. Material systems include glasses for spacecraft windows, thermal barrier coatings, and aluminum nitride substrates. Microstructural stresses related to enhanced fracture toughness and damage mechanisms are measured via micro-Raman techniques in heterogeneous microstructures and correlated with micro-mechanical modeling. Micro-mechanical computer simulations are used to elucidate distributions of residual stresses and microcrack damage in highly anisotropic ceramics as a function of crystallographic texture. At elevated temperatures, the basic mechanisms responsible for crack growth, creep, and creep-rupture are investigated for various silicon nitride compositions, and for membrane and fuel cell materials.

To improve interlaboratory comparisons and to increase confidence in generated data, new standard test techniques for hardness, strength, and toughness are being developed and tested in round robin experiments. Research and interlaboratory studies in instrumented indentation address the use of this technique for measuring elasticity and hardness of thin films and coatings. Micro-Raman techniques are being developed and calibrated so that quantitative assessments of microstructural residual stresses can be mapped for heterogeneous microstructures. At elevated temperatures, new creep specimens are designed which permit higher stresses with reduced non-gage section failures. Intra- and inter-laboratory studies demonstrated the robustness of these geometries. International inter-laboratory studies are underway to elucidate their relationship to alternate testing geometries.

Finally, techniques to predict lifetimes of ceramic materials and glasses under constant and variable loading conditions are being developed. A nonparametric bootstrap approach for assessing the confidence of lifetime predictions is investigated and compared with analytical techniques. Work includes applying these techniques to fused silica and other glasses for spacecraft window applications. A new experimental procedure is being explored for characterizing time-dependent failure under static loads.

PROGRAM TITLE: Mechanical Properties of Brittle Materials

PROJECT TITLE: High-Temperature Creep and Reliability

Principal Investigators: Ralph Krause, Jr., William E. Luecke, and Sheldon M. Wiederhorn (850)

Technical Objectives:

This research is designed to assist industry in the evaluation, design, and development of advanced structural ceramics for use as high-temperature components in land-based heat engines for power generation and vehicles, and in the development of measurement methodologies for the evaluation of the necessary high-temperature mechanical properties.

Technical Description:

The mechanisms and statistics of high temperature creep and rupture in advanced ceramics have been studied and test methods for these measurements have been developed and refined. The results have been used to elaborate microstucture-based models of creep and failure. Using extensive creep facilities (9 tensile, 3 compression, and 6 flexure machines) the data necessary to make databases that allow statistical interpretations of creep can be obtained. In addition, scientists from industry and academia use these facilities.

External Collaborations:

Frantisek Lofaj, Slovak Academy of Sciences
Chien-Wei Li, AlliedSignal
David Wilkinson, McMaster University
Wolfgang Braue, German Aerospace Research Establishment
Prof. Georg Grathwohl, Technical University of Bremen
Prof. Nitin Padture of the University of Connecticut
Prof Jürgen Rödel of the Technical University of Darmstadt

Planned Outcomes:

- Uncertainties in lifetime inherent to these models will be examined, for incorporation in to fracture mechanism maps. The fracture mechanism maps and related confidence limits will be used for component life prediction.
- More accurate, microstructure-based models for creep of silicon nitride and other structural ceramics that are bonded by a less-ductile silicate phase will be developed.

Accomplishments:

The round robin for tensile creep of silicon nitride begun in 1998 is complete. Different laboratories produced times to failure that varied by nearly a factor of 100, strains to failure that varied by up to five times, and minimum creep rates that ranged over more than ten times. The

results of this study have been summarized in a precision and bias statement that will be balloted for incorporation in the ASTM standard for tensile creep of advanced ceramics during Fall 1999.

In collaboration with AlliedSignal a new grade of silicon nitride for structural applications is being characterized. This material shows the highest apparent activation energy for creep ever measured in this lab.

Anomalies between predicted and measured cavitation behavior of a new grade of silicon nitride have been detected. These anomalies have important implications in extrapolating observed creep behavior to low stress and long times.

MSEL visiting scientist, F. Lofaj, has developed new relations and techniques for characterizing cavitation damage in silicon nitride using sound velocity measurements.

A pure-shear creep specimen has been developed for testing the possibility of cavitation damage in shear deformation of silicon nitride. Currently, no shear deformation data at large strains exists for silicon nitride, despite 20 years of elevated temperature testing.

Publications:

Qiang Jin, David S. Wilkinson, George C. Weatherly, William E. Luecke, and Sheldon M. Wiederhorn, "Viscous Flow Creep in Ceramics Containing Secondary Crystalline Phases" *Acta Mater.* in press (1999).

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William E. Luecke and Sheldon M. Wiederhorn, "A New Model for Tensile Creep of Silicon Nitride," *J. Am Ceram. Soc.*, **publication expected, Oct** (1999).

Robert P. Jensen, William E. Luecke, Nitin P. Padture, and Sheldon M. Wiederhorn, "High-Temperature Properties of Liquid-Phase-Sintered α-SiC," submitted to *Materials Science and Engineering A*, September 1999.

R.F. Krause, Jr., "Estimation of Characteristic Parameters of a Grain-Bridging Model for Crack-Extension Resistance," *J. Am. Ceram. Soc.*, **82** 373-79 (1999).

R.F. Krause, Jr., S.M. Wiederhorn, and J.J. Kuebler, "Misalignment Induced
Bending in Pin-Loaded Tensile Creep Specimens," submitted to *J. Am. Ceram. Soc.*, August 1999.

S.M. Wiederhorn, B.J. Hockey and J.D. French, "Mechanisms of Deformation of Silicon Nitride and Silicon Carbide at High Temperatures," *J. Eur. Ceram. Soc.* in press (1999)

S.M. Wiederhorn and W.E. Luecke, "Creep of Silicon Nitride," pp. 3-17 in Computer Aided Design of High Temperature Materials, A. Pechenik, R.K. Kalia and P. Vashishta, eds. Oxford University Press, Oxford, UK (1999).

PROGRAM TITLE: Mechanical Properties of Brittle Materials

PROJECT TITLE: Mechanical Property Modeling

Principal Investigators: Andrew R. Roosen, Stephen A. Langer [Mathematical and Computational Sciences Division (891), ITL], and Edwin R. Fuller, Jr.

Technical Objectives:

This research is designed to assist industry through the development of new paradigms for elucidating micro-physical behavior of real and simulated material microstructures. Theoretical and computational methods are applied to bitmap images to investigate microstructural stresses and strains, fracture, deformation and damage behavior, ferroelectric domain switching, and other nonlinear phenomena in polycrystalline and multi-phase ceramics and ceramic composites. A particular objective is the creation of tools for the prediction and computation of behaviors in real microstructures with the aim of identification of microstructural features that optimize macroscopic properties in commercial materials. The goal is the development of a generalized set of tools, which all materials scientists can and will want to use.

Technical Description:

Microstructures in real materials are complex objects, which can contain distributed second phases, each having their own localized constitutive behavior. Microstructures can also contain cracks, pores, and other features, which severely affect performance. A general software tool, called ***OOF*** (for **O**bject **O**riented **F**inite Elements) is being developed which incorporates all such complexity and which organizes local constitutive behavior so that calculations can be performed in systems that would otherwise be intractable. The research models the mechanics and physics of heterogeneous microstructures at the microscopic level.

External Collaborations:

This research involves numerous external collaborations. Informal joint projects include:

- Donald M. Baskin and Prof. Katherine T. Faber
  Department of Materials Science and Engineering
  Northwestern University, Evanston, IL
- André Zimmermann and Prof. Jürgen Rödel
  Fachgebiete Nichtmetallisch-Anorganische Werkstoffe
  Technische Universität Darmstadt, Darmstadt, GERMANY
- Stefan Lampenscherf, Dr. Manfred Bobeth, and Prof. Wolfgang Pompe
  Institut für Werkstoffwissenschaft
  Technische Universität Dresden, Dresden, Germany

- Prof. W. Craig Carter
  Department of Materials Science and Engineering
  Massachusetts Institute of Technology, Cambridge, MA
- Drs. Venkata R. Vedula and S. Jill Glass
  Sandia National Laboratories, Albuquerque, NM
- Prof. Anil Saigal
  Department of Mechanical Engineering, Tufts University, Medford, MA
- Drs. Chun-Hway Hsueh and Paul Becher
  Metals and Ceramics Division, Oak Ridge National Laboratory, Oak Ridge, TN
- Prof. Vinayak P. Dravid
  Department of Materials Science and Engineering
  Northwestern University, Evanston, Illinois

Additionally, more than three hundred researchers have down-loaded the ***OOF*** software from the CTCMS (Center for Theoretical and Computational Materials Science) Software archives, are using ***OOF***, and providing us feedback. The ***OOF*** mailing list has over 100 subscribers.

Planned Outcomes:

That ***OOF*** will become a new paradigm for computation on real microstructures and will aid in the development and prediction of commercial materials through virtual materials testing.

Accomplishments:

Version 1.0 of ***OOF*** was released as public domain software. ***OOF*** is easy to use, having a graphical interface. It performs several tasks:

- Combines microstructural image data with materials data and constitutive behavior.
- Applies (virtual) experimental boundary conditions and/or stress-free localized strains.
- Solves for thermoelastic stresses and strain fields.
- Predicts and incorporates materials damage.
- Quantifies and visualizes results.

OOF uses image data from real or simulated materials to create a finite element mesh. The program includes tools for selecting and manipulating features in an image, a finite-element mesher and solver, and an extensive interface.

A description of ***OOF***, links to the first publicly released version of the program, which may be downloaded as public-domain software, an interactive manual, and a "Picture and Simulation Gallery" are available on the Internet at URL address:

http://www.ctcms.nist.gov/oof/

Thus far, more than 300 copies of the program have been downloaded.

Specific accomplishments include:

- Version 1.0 released, and manual published.
- Wider range of material constitutive behaviors incorporated.

- New image modification tools implemented.
- New meshing schemes, including a novel adaptive meshing tool, introduced.
- New visualization and analysis tools developed.
- Ported to Sun workstation and PC running Linux.
- Development of Version 2.0 began.
- Simulations of residual stress distributions and microcrack damage generation in polycrystalline ceramics, of residual stresses in thermal barrier coatings resulting from interface roughness and a thermally grown interface oxide, and of damage shear-band generation in compressive thin films with heterogeneities.

Publications:

An on-line *OOF* Manual, URL address:
http://www.ctcms.nist.gov/~langer/oof/Manual/Manual.html

The OOF Manual: Version 1.0, NISTIR 6256.

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Anil Saigal, E. R. Fuller, Jr., S. A. Langer, W. C. Carter, M. H. Zimmerman, and K. T. Faber, "Effect of Interface Properties on Microcracking of Iron Titanate," *Scripta Materialia*, **38** [9], 1449-1453 (April 3, 1998).

C.-H. Hsueh, P. F. Becher, E. R. Fuller, S. A. Langer, and W. C. Carter, "Analytical and Numerical Analyses for Two-Dimensional Stress Transfer," Mater. Sci. Eng., submitted.

Anil Saigal and E. R. Fuller, Jr., "Analysis of Stresses in Aluminum-Silicon Alloys," Computational Materials Science, submitted.

Chun-Hway Hsueh, James A. Haynes, Michael J. Lance, Paul F. Becher, Mattison K. Ferber, Edwin R. Fuller, Jr., Stephen A. Langer, W. Craig Carter, and W. Roger Cannon, "Effects of Interface Roughness on Residual Stresses in Thermal Barrier Coatings," J. Am. Ceram. Soc., **82** [4], 1073-1075 (Apr. 1999).

Donald Matthew Baskin, "Fracture Behavior of Single Phase Iron Titanate Laminate Composites," Ph.D. Dissertation, Northwestern University, June 1999.

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André Zimmermann, Edwin R. Fuller, Jr., and W. Craig Carter, "Damage Evolution During Microcrack Formation in Brittle Solids," *Acta Materialia*, submitted June 1999.

Chun-Hway Hsueh and Edwin R. Fuller, Jr., "Residual Stresses in Thermal Barrier Coatings: Effects of Interface Asperity Curvature/Height and Oxide Thickness," Mater. Sci. Eng., submitted, September 1999.

Chun-Hway Hsueh and Edwin R. Fuller, Jr., "Residual Stresses in Thermal Barrier Coatings: Analytical Modeling of Oxide Thickness Effects," *Scripta Materialia*, submitted, September 1999.

PROGRAM TITLE: Mechanical Properties of Brittle Materials

PROJECT TITLE: Mechanical Test Development

Principal Investigator: George D. Quinn

Technical Objectives:

Procedures are developed for characterizing ceramics and standard test methods are prepared for ASTM and ISO consideration. Our goal is to develop procedures that are as technically rigorous as possible while remaining practical and useable by industry.

Technical Description:

Mechanical testing methods for ceramics are created, improved, refined, and standardized. Hands on testing is conducted to gain first-hand experience with a method. Upon reaching a mature prestandardization level, a method is evaluated by round robin(s) which verify the suitability of the method and generate precision and bias data. Foundation work for standard reference materials is performed. Current work is targeted towards fracture toughness, hardness, diametral compression strength, and flexure strength (cylindrical specimens) tests.

External Collaborations:

Industry is consulted for test method standardization needs (e.g., Cummins). The Department of Energy, Office of Heavy Vehicle Technologies, provides programmatic support for some portions of this project. ASTM Committees such as C-28, Advanced Ceramics, E-28 Mechanical Testing, E-08 Fracture and Fatigue, and F-04 Surgical and Medical Devices are consulted and used as forums for creating standards. International collaborations are maintained through the VAMAS program and other fora. International standardization is pursued through ISO Technical Committee 206, Fine Ceramics and contacts in CEN Technical Committee TC 184, Advanced Technical Ceramics.

Planned Outcomes:

Standard practices or test methods are prepared so that accurate and precise mechanical property data can be obtained by NIST, industry, government, and academia. Emphasis is on preparing ASTM and ISO standards. This project also serves as a lead into Standard Reference Material projects. VAMAS round robin projects are conducted as necessary to verify test method maturity.

Accomplishments:

ASTM standard C 1421-99 Standard Test Method for Determination of Fracture Toughness of Advanced Ceramcs at Ambient Temperatures was adopted in April 1999. The standard actually is three separate test methods combined into one super standard and thus bears some similarity to

the master fracture toughness of metals standard, E 399. Each of the 3 test methods within C 1421 was refined through years of work supported by 5 major international VAMAS round robins with thousands of experiments conducted by over 40 laboratories. Throughout the period of C 1421's development, the state of the art of fracture resistance testing and our fundamental understanding of R-curves was evolving. C 1421 is a high quality, technically rigorous ASTM standard. One may obtain identical fracture toughness results from the 3 methods in the standard for simple microstructure monolithic ceramics (i.e. flat R-curve materials). This work was done in cooperation with Prof. I. Bar-On of Worcester Polytechnic, Prof. M. Jenkins of the University of Washington, and Dr. J. Salem of NASA-Lewis.

In tandem with the creation of C1421-99, NIST created a *Standard Reference Material: SRM 2100 Ceramic Fracture Toughness* is the very first fracture toughness reference material in the world for any class material. Any one of the three test methods in ASTM C 1421 (or any other method the user chooses as long as it relies on a flexure specimen) may be used on the SRM specimens. The specimens in SRM 2100 have an average fracture toughness of 4.57 MPa$\sqrt{m}$. The 95% confidence bounds for the average fracture toughness of the 5 test specimens in the SRM kit is only 0.11 MPa$\sqrt{m}$, which is only of 2.4% of the mean fracture toughness. Since the three independent test methods in C 1421 yield identical results on the SRM specimens, one is led to believe that the true toughness is indeed 4.57 MPa$\sqrt{m}$ with a precision of better than 1% in the basis of the large NIST data base for SRM 2100. Thus, SRM 2100 is an unusually accurate and precise SRM.

Rolling Element Bearing Group Silicon Nitride Material Specification

In 1999, we participated in the Rolling Element Bearing Group (REBG) subcommittee on ceramic bearing balls. REBG, an association of Department of Defense and bearing manufacturers and users, is preparing a silicon nitride material specification for bearing balls. The specification has three classes or grades of silicon nitride, depending upon material purity, strength, Weibull modulus, hardness, fracture resistance, and other properties. The REBG specification uses 10 ASTM standards as possible methods for measuring the properties in order to classify the material. Six of the ASTM standards were created (or co-authored) by NIST in the last 9 years.

Three materials specification standards have been created in ASTM committee F-04, Surgical and Medical Devices, to cover alumina, yttria partially stabilized zirconia, and magnesia partially stabilized zirconia in 1998-1999. these medical materials specifications also refer and use to the ASTM Committee C-28 generic test method standards for hardness, flexure strength and Weibull modulus.

These examples demonstate that, the generic test methods standards are now being used as building blocks to craft materials specification standards. It is gratifying to observe our generic test method work being used so gainfully to enhance commercialization of advanced ceramics.

ISO Technical Committee TC 206, Fine Ceramics

Work in this project contributed to four Working Groups (WG) in this ISO TC.

Working Group 2, Flexural Strength The US - NIST leads this WG and we prepared a new draft ISO standard document which is currently being balloted as "Final Draft International Standard."
Working Group 7, Fracture Toughness by SEPB NIST worked with the USA task group in responding to the Japanese draft.

Working Group 8, Flexure Strength at Elevated Temperatures The US -NIST leads this WG. A complete first draft was prepared and has been approved for balloting as a "Committee Draft."

Working Group 16, Fracture Toughness by SCF NIST prepared a formal draft and TC approved the establishment of this WG.

VAMAS Technical Working Area 3, Ceramics Projects

1999 again was busy year for TWA #3. Mr. Quinn is the chairman of TWA #3. Meetings were held in Brighton, United Kingdom. One round robin is nearing completion, another is juts getting started, and as many as 6 new proposals have been received!

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Fracture Toughness by The SEVNB method organized by EMPA - Jacob Kübler, Switzerland. This project featured an innovative simple method to precrack specimens with a razor blade and diamond paste. NIST participated and aided in the review of the final report. It appears that this simple means of producing a sharp notch (saw cut sharpened by an ordinary razor blade with diamond paste) is very effective. This method probably will be on a fast track for standardization.

Flexure Strength at Elevated Temperatures organized by the Japan Fine Ceramic Center. As of October 1999, 13 laboratories have agreed to participate. In the United States, NASA-Lewis and Oak Ridge National Lab have subscribed. The Japanese have organized this round robin to investigate several issues that concern them in connection with the ISO Technical Committee TC 206 draft standard.

Impacts:

This project has had a great impact on the ceramics community. The work is vertically integrated. Test method research at NIST evolves into VAMAS prestandardization round robins, to ASTM standards, to NIST SRM's, and eventually into worldwide ISO standards. Refined and standardized test methods are now available. Data quality has improved dramatically, both for routine characterization and design purposes. It is easy to compare data between laboratories. ASTM C-28 standards are now being cloned by other Committees. Tangible benefits include significant cost savings to USA industry. For example, over $1M per year is saved by the USA by the use of standardized bend bars. The standards are being combined in materials specifications. Standards also convert loose research procedures into mature engineering practices. For example, the C-28 fractographic analysis standard, C 1322, codified and demystified what heretofore had been a highly interpretive "black art." C 1322 now is used as a teaching aid in courses at several universities and by a course offered by the American Ceramic Society. New scientific knowledge has emerged from prestandardization work such as the

entirely new concept for brittleness which was discovered during our conventional hardness prestandardization research. The work in this project also supports USA trade by maintaining a lead role in International Standardization fora.

Publications:

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W. Kanematsu, M. Sando, L. Ives, R. Marinenko, and G. Quinn, "Determination of Machining Crack Geometry by Dye Penetration Technique," submitted to JACS, 1999.

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G. D. Quinn, "VAMAS After Twelve," Bul. Amer. Ceram. Soc., Vol. 78, No. 7, July 1999, 78-83.

PROGRAM TITLE: Mechanical Properties of Brittle Materials

Project Title: Instrumented Indentation

Principle Investigators: Douglas T. Smith and Jay S. Wallace

Technical Objectives:

1. To organize workshops and symposia that will bring the instrumented indentation community towards consensus on recommended test and analysis procedures, and to participate in indentation round robins; and, in conjunction with other standards laboratories Bundesministerium für Wirtsschaft (BAM), and National Physical Laboratory (NPL), to prepare and characterize possible candidates for coating-substrate standard reference materials (SRM's) for mechanical testing.

2. To collect experimental indentation data (load-displacement curves) and correlate them with analytical and numerical modeling of the indentation process, in order to better understand deformation mechanisms beneath indenters, particularly in film-substrate and multilayer systems.

3. To use instrumented indentation to quantify hardness, Young's modulus, porosity and microcrack density in ceramic coatings, both to characterize as-prepared coatings and to quantify damage evolution. Also, to study the microstructural damage done during the indentation of brittle coatings and bulk material and, when possible, to correlate that damage with other material properties such as machinability, thermal fatigue and wear resistance that depend on microfracture processes.

4. To investigate the effect of changing fabrication conditions and post fabrication annealing on the elastic modulus of free standing air plasma sprayed ZrO_2 deposits and correlate these changes with changes in microstructure found by small angle neutron scattering and scanning electron microscopy. Also, to study the changes in phase composition which are the result high temperature annealing and correlate these changes with neutron diffraction measurements.

Technical Description:

The program uses two instrumented indenters (one a commercial nanoindenter and one a NIST-modified microhardness machine) to probe the mechanical properties of bulk materials and thin films. Taken together, the two machines permit indentation studies at peak indentation loads ranging from 40 μN to 40 N, using Vickers, Berkovich and spherical diamond and WC-Co indenter tips. The resulting experimental load-displacement curves are analyzed to yield the hardness and Young's modulus of the material probed, as well as the energy absorbed in the indentation process. Since elastic modulus measurements are sensitive to discontinuities in the microstructure, such as cracks and crack-like voids, they are well suited to the study of changes that occur as the result of changing fabrication conditions or post-fabrication treatments. Relatively small areas of material are probed, permitting local mapping of elastic modulus variations.

The focus of the program is on the development of the *technique* of instrumented indentation, rather than the application of the technique to particular material systems, although data are taken on specific materials of technological interest (*e.g.*, thermal barrier and wear-resistant coatings), as well as candidates for Standard Reference Materials. International workshops, symposia, and round robin standards tests are organized and executed in an effort to guide the instrumented indentation community toward greater standardization in data analysis, to the expand the range of mechanical property characterization possible with the technique, and to develop physical standards for the technique.

External Collaborations:

1. National Physical Laboratory (NPL), U.K., and Tokyo University, Japan: Design and execution of VAMAS instrumented indentation round robin testing of model film-substrate systems.

2. ASTM Task Group E28.06.11. Development of ASTM standard test practices and methods for instrumented indentation testing (IIT).

3. Federal Institute for Materials Research and Testing (BAM), Berlin: Development of reference coatings using indentation and spectroscopic ellipsometry.

4. Institute of Plasma Physics, Academy of Sciences of the Czech Republic: Study of processing and property evolution of free standing air plasma sprayed ZrO_2 deposits.

5. Department of Material Science and Bioengineering, Agency of Industrial Science and Technology (AIST) and Ministry of International Trade and Industry (MITI), Japan: Study of functionally graded materials prepared by plasma arc sintering.

Planned Outcomes:

Recommended guidelines and standard test practices and methods for instrumented indentation testing and analysis procedures will help researchers with different indentation systems at different laboratories compare results effectively. Bulk and film standard reference materials and ASTM standards will aid in machine operation, calibration and verification.

Reliable mechanical property data at small length scales will aid designers of thin-film and multilayer structures.

Changes in the crack/void structure of plasma sprayed thermal barrier coatings, due either to changing processing conditions or in service annealing, can have a significant influence on the resulting properties, and thus must be well characterized and understood. Instrumented indentation measurements provide a sound basis for characterizing and quantifying these changes.

The use of instrumented indentation to introduce and quantify microcrack damage may lead to the use of the technique to predict thermal fatigue behavior, wear resistance and fracture toughness.

Accomplishments:

In collaboration with the National Physical Laboratory in England and Tokyo University, a new VAMAS Technical Working Area has been started (TWA 22: Mechanical Properties of Thin Coatings), and the first project is well under way (Hardness and Modulus Measurement Using Depth Sensing Indentation). Sets of film/substrate specimens have been distributed and tested, and results are being analyzed. In addition, an new project is beginning on thin film adhesion testing.

Extensive measurements have been made of the mechanical properties of several zirconia air-plasma-sprayed thermal barrier coatings, studying both the influence of feedstock powder characteristics as well as the response of the deposit to thermal treatments. The focus of the work is correlation of elastic modulus changes, measured by instrumented indentation, with microstructural changes, measured with scanning electron microscopy (SEM) and small angle neutron scattering (SANS). Direct SEM observations have shown that the fine cracks within splats are the first to heal during annealing. The removal of these cracks results in a large increase in measured elastic modulus with only minor changes in the density of the deposit. These observations have been confirmed by SANS measurements. Also, preliminary measurements have shown that, as long as the feedstock particles are melted during deposition, the properties of the deposit are primarily controlled by the mean particle size and are relatively insensitive to the width of the particle size distribution. Long-term annealing experiments, coupled with neutron diffraction and instrumented indentation measurements, are being used to determine the phase and damage evolution in these materials.

One symposium on mechanical property testing for coatings was held as part of the International Conference on Metallurgical Coatings and Thin Films, April, 1999, in San Diego. Another is currently being organized for April, 2000. An ASTM workshop on the technique was held on November 4, 1998, at an ASTM meeting in Norfolk, VA.

Publications:

U. Beck, D.T. Smith, G. Reiners and S.J. Dapkunas, "Mechanical Properties of SiO_2 and Si_3N_4 Coatings: A BAM/NIST Cooperative Project," *Thin Solid Films* **332**, 164-171 (1998).

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PROGRAM TITLE: Mechanical Properties of Brittle Materials

PROJECT TITLE: Test Development for Membrane Materials

Principal Investigators: William E. Luecke, Ralph Krause, Jr., Tze-jer Chuang, and Jay Wallace

Technical Objectives:

Develop mechanical property measurement techniques for dual-purpose oxygen-conducting ceramics. Apply these techniques to understand deformation, degradation, and failure mechanisms of these ceramics, thereby improving their reliability.

Technical Description:

High-temperature deformation of $(La,Sr)(Ga,Mg)O_3$ is being investigated. Thermal cycle tests that simulate use conditions are being used to elucidate damage accumulation processes at temperatures less than 800 °C. Probing the local change in elastic modulus during cycling, using instrumented indentation, will allow mapping of the damage generated during thermal cycling. Eventually, the failure mechanisms determined in these tests will be linked to more formal tests of subcritical crack growth. Finally, because these materials will frequently be used in tubular form, strength tests based on tubular geometry have been developed. Therefore, this simple, easily available geometry can be used to generate data necessary for low-temperature reliability calculations.

External Collaborations:

Dr. Timothy Armstrong, Oak Ridge National Laboratory
Prof. Allan Bower, Brown University

Planned Outcomes:

- Develop predictive models for creep of doped lanthanum gallate
- Refine the O-ring strength test, and establish limits of validity
- Develop instrumented hertzian indentation as a method for characterizing the spatial and temporal variability of damage due to thermal cycling in membrane materials.

Accomplishments:

The elevated temperature failure mechanisms of dual-purpose oxygen-conducting ceramics has been investigated. In service, these materials will experience long periods at high temperatures (500 °C to 1000 °C) under load, as well as thermal stresses induced during startup and shutdown. They may fail by one of several possible mechanisms. Creep, or the slow deformation under load dominates at the highest temperatures, characteristic of steady-state conditions. At lower temperatures and higher stresses, it is possible that pre-existing flaws may extend due to subcritical crack growth. Thermal cycling during startup and shutdown induces stresses that may

nucleate new flaws, that can extend to failure even at room temperature, if stresses are too high, spontaneous failure can occur. Ensuring reliability of candidate materials in service requires the understanding of all of these failure mechanisms. Models for the failure processes must be based on sound, microstructurally based materials science.

The creep behavior of a candidate second-generation fuel cell electrolyte, $(La,Sr)(Ga,Mg)O_3$ has been characterized and found to be slightly less creep resistant than the ZrO_2 currently used in solid-electrolyte fuel cells. In parallel, models for transient growth of pores in ceramics subjected to tensile stresses have been developed.

An automated, indexable microindentation apparatus for characterizing the spatial distribution of elastic modulus in flat specimens has been built. Using this equipment, the degradation in modulus of a specimen of $LaGaO_3$ resulting from thermal cycling between room temperature and the expected service temperature of 800 °C was followed. These tests establish that subcritical crack growth occurs during thermal cycling, which ultimately leads to material failure.

The effect of specimen size on ring strength was investigated. The specimens differed by outside diameter, length, and wall thickness. A simple loading fixture was fabricated to provide diametric loading uniformly along the specimen length. Preliminary Weibull distributions have been obtained from 4 groups of 10 specimens in each group. The groups differ in the ratio of the diameter, length, or wall thickness, by a factor of two, respectively. Strength was calculated both by an analytical approximation and a Fourier series expansion. The approximation method gave values generally 5 % less than those by the expansion method.

PHASE EQUILIBRIA FOR CERAMICS AND METALS

Thermodynamic phase equilibrium data, which indicate the identities and quantities of the final, stable products of any given process, are essential tools for developers and manufacturers of engineering materials. The Phase Equilibria Program encompasses not only data compilations and experimental measurements of phase equilibria, but also development of thermodynamic and first-principles models which form the underlying basis of the equilibria. In addition, several projects go beyond the direct graphical representation of equilibria to include characterization of the physical and crystallographic properties of the constituent phases, or to incorporate the equilibrium information into kinetic models of non-equilibrium processes. MSEL phase equilibrium work includes the following main projects:

High Temperature Superconductors

The objective of this activity is to conduct experimental studies of copper-based materials with emphasis on regions and conditions pertinent to the improved manufacture of bulk superconducting wires and tapes. Efforts have been largely directed to the Bi-Sr-Cu-Ca-O systems which are currently of greatest commercial interest. The successful processing of wires with high current-carrying capacities and excellent superconducting properties is known to require the *in situ* coexistence of high quality superconducting solid plus a liquid phase to induce texturing and grain alignment. The phase diagram work is therefore directed toward determining the location in composition-P-T space of the primary crystallization fields of the BiSCCO superconductors; that is, the regions where only two phases are present - the superconducting solid plus a liquid. In addition, work is in progress to develop graphical and other practical methods for end users of the complex data. Recently, work has been initiated on selected $YBa_2Cu_3O_7$-type systems of interest for the development of coated conductors. For these cuprate superconductors, information is needed on phase equilibria relations at low oxygen partial pressures similar to those encountered in deposition chambers. This research is carried out in close collaboration with the U.S. Department of Energy (DOE) Superconductivity Program for Electric Systems and its participating national laboratories.

Dielectrics for Wireless Communications

Dielectric ceramics are used to fabricate a variety of components in cellular communications circuits that store, filter, and/or transfer electromagnetic energy with minimal loss (e.g., resonators, bandpass filters, circulators). The required properties for the ceramic materials include high dielectric constant, minimal dielectric loss, and essentially zero temperature dependence of dielectric properties. Knowledge of phase equilibria relations is important because all ceramic components are processed as controlled mixtures to achieve temperature stabilization; furthermore, the existence of previously unknown compounds with potentially useful properties may be revealed. This research activity emphasizes experimental determination of ternary (or higher) phase diagrams that contain one or more components or compounds that exhibit useful properties, and the correlation of chemical composition, atomic arrangement, and dielectric performance within each system. The experimental work includes synthesis, structural analysis, determination of phase relations, and microwave characterization (via collaborators at NIST-Boulder) of dielectric properties.

Computational Studies of Ferroelectrics and Dielectrics

Ferroelectric ceramics exhibit unique dielectric properties that are widely exploited to produce multilayer capacitors and transducers. Related ceramic systems are useful as high performance dielectric resonators for wireless communications. The electronic properties of these materials are strongly dependent on the exact ordering patterns adopted by the atoms within the ceramic material; only certain, precise arrangements result in electronically useful properties. Understanding of why and how these particular arrangements occur is needed by industry to improve processing control, reduce the associated costs, and enable the rational design of improved materials. The objective of this research activity is to develop and apply computational tools to model the structural behavior of these important materials as a function of chemical composition and temperature. The work is carried out using first principles phase diagram calculations, including the Ising model and Monte Carlo methods.

NIST-ACerS Phase Equilibria Diagrams Database

The objective of this project is to prepare and publish evaluated phase equilibria data for the industrial and academic communities. Technical evaluation of original literature containing phase diagram information is carried out under NIST supervision. The preparation of the evaluated diagrams for dissemination as the reference series, Phase Equilibria Diagrams (formerly Phase Diagrams for Ceramists), is conducted at NIST in collaboration with on-site personnel of the American Ceramic Society (ACerS). The ACerS personnel are primarily supported by funds raised by the Society from industry, academia, and individuals. The collaboration represents an over-60-year agreement with ACerS to provide technically evaluated phase diagrams for the ceramics industry.

Data for Pb-Free Solders

Thermodynamic phase diagram modeling has been performed for potential Pb-free solders in the Sn-Ag-Bi-Cu quaternary system. Through extrapolation of binary and ternary subsystems and selected critical measurements, the Sn-Ag-Bi-Cu quaternary system has been predicted. Thus, important alloy characteristics such as liquidus temperature, melting range, and phase content can be predicted. These predictions are being used by industrial partners to down-select compositions for further study on wettability and thermomechanical fatigue resistance. This work continues efforts initiated under a completed NCMS consortium project on lead-free alloys, and involves many of the same industrial partners under a National Electronics Manufacturing Initiative (NEMI). NIST work on lead-free solders has been made publicly available through NCMS, providing technical information needed by industry and government bodies considering replacement of lead-containing solders. An internet resource for Pb-free solder data is planned.

PROGRAM TITLE: Phase Equilibria for Ceramics and Metals

PROJECT TITLE: Computational Studies of Ferroelectrics and Dielectrics

Principal Investigator: B.P. Burton and E.J. Cockayne

Technical Objectives:

The objective of this project is to elucidate the roles of cation order-disorder and ferroelastic phenomena in dictating the phase relations, and physical properties, of technologically important electronic materials. Typically, these materials are ceramic compounds with exploitable ferroelectric, dielectric, or magnetic properties, and are widely used in technical applications such as actuators, transducers, or dielectric resonators.

Technical Description:

Ferroelectric, dielectric, magnetic, and transport properties of these materials are typically sensitive functions of the state of cation order; therefore, First-Principles Phase Diagram (FPPD) calculations are used to predict cation ordering phenomena, physical properties, and how they vary with chemical composition. Critical experiments are performed to test the predictions. An additional technical objective is to benchmark various FPPD techniques that are used for calculating physical properties (e.g. dielectric constant), and the formation energies on which FPPD calculations are based.

External Collaborations:

A working group has been formed to develop a unified effective Hamiltonian for modeling systems that exhibit both cation order-disorder and ferroelastic transitions. Group members are B.P. Burton and E. Cockayne (NIST); K.M. Rabe (Rutgers); L. Bellaiche (U. Arkansas); N.A. Hill (UCSB); G. Ceder (MIT); Mark Asta (Northwestern); and U. Wagmare (Harvard).

Other collaborators in this work include:

G. Ceder and A. Van Der Ven (MIT): issues related to Ising model calculations.

K. M. Rabe and Ph. Ghosez (Yale): pseudopotentials and first-principles methods for calculating total energies and linear responses.

J. B. Aidun, T. V. Russo and K. Leung (Sandia): FPPD calculations for the $PbTiO_3$-$PbZrO_3$ system.

Planned Outcomes:

The intended outcome is to predict ordering behavior in complex technologically important oxide systems, with the objectives of: (1) minimizing the experimental work necessary to elucidate phase relations; (2) optimizing theoretical techniques; (3) optimizing processing strategies for these materials; (4) predicting the existence of new, technologically relevant ordered phases; (5) predicting how physical properties vary as functions of composition and temperature.

The inclusion of degrees of freedom, derived from ionic motion, in the first-principles models will facilitate simulation and physical understanding of important properties. For example, the ferroelastic transitions in PZT, experimentally associated with large piezoelectricity, can be simulated as a function of temperature and strain. By adding the effects of time-varying external fields to the models, dielectric response as a function of temperature and frequency can be modeled in systems such as $CaTiO_3$-$Ca(Al_{1/2}Nb_{1/2})O_3$

Accomplishments:

The different roles of long-range Coulomb interactions and short-range Pb-O bonding in stabilizing cation ordered perovskite derivatives have been elucidated. The phases studied include Ba perovskites and disordered phases in the corresponding Pb-perovskites.

We are working on extending the first-principles effective Hamiltonian method for computing phase transitions and electromechanical properties of oxides to the case of a system ($PbZrO_3$) with competing ferroelectric and antiferroelectric lattice instabilities. We have explained why $PbZrO_3$ and Zr-rich $PbZr_{1-x}Ti_xO_3$ exhibit phase transformation behaviors under pressure which are different from those of the related compound $PbTiO_3$.

A method has been introduced whereby first principles models and EXAFS experiments can work in tandem to determine the local structure in a solid solution. In the case of $Pb_{1-x}Ge_xTe$, good agreement was found between structural parameters fit to first principles calculations and those determined experimentally.

Preliminary results have been obtained on first-principles computation of phonon modes and static dielectric constants for $CaTiO_3$ and $CaAl_{1/2}Nb_{1/2}O_3$. To our knowledge, these are the first first-principles studies of the phonons in a 20 atom-per-cell oxide. The preliminary results show that the large dielectric constant in $CaTiO_3$ arises primarily from a set of low-frequency vibrations in which the cations move in a direction opposite that of the oxygen ions. The corresponding modes in $CaAl_{1/2}Nb_{1/2}O_3$ involve Al and Nb moving in opposition to Ca, thus suppressing the total dielectric response and dielectric constant.

A sphere packing has been discovered which is the densest known quasicrystalline arrangement (i.e. packing fraction higher than body centered cubic); proof of mechanically stability has also been demonstrated. A new cluster model for quasicrystals, which sheds light on the quasi-unit-cell picture for quasicrystals, has also been devised.

Publications:

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E. Cockayne and K.M. Rabe, "Pressure Dependence of Instabilities in Perovskite $PbZrO_3$", J. Phys. Chem. Solids (in press).

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B. Ravel, E. Cockayne, K. M. Rabe, and M. Newville, "A Combined EXAFS and First-Principles Study of $Pb_{1-x}Ge_xTe$", Phys. Rev. B (in press).

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PROGRAM TITLE: Phase Equilibria for Ceramics and Metals

PROJECT TITLE: Dielectric Oxides for Wireless Communications

Principal Investigator: T.A. Vanderah

Technical Objectives:

The objective of this project is to conduct experimental studies of phase equilibria and structure-property relations in complex titanate- and niobate-based systems of interest as dielectric oxides in wireless communications systems.

Technical Description:

Every modern commercial wireless communication and detection system either under deployment or advanced development incorporates dielectric oxide ceramics with unique electrical properties as critical elements. These materials are used to fabricate a variety of components in cellular communications circuits that store, filter, and/or transfer electromagnetic energy with minimal loss (e.g., resonators (bandpass filters), circulators). The required properties for this class of ceramics include high dielectric constant, minimal dielectric loss (which precludes the use of ferroelectric oxides), and essentially zero temperature dependence of dielectric properties. All of the ceramic systems currently in use were empirically "discovered", and essentially no fundamental knowledge exists of why and when this unique set of properties occurs. This lack of basic understanding, which could result in better control of processing, and better design of ceramics with enhanced performance, has been identified by U.S. industry as the most important R&D materials issue for this class of electronic materials with regards to global commercial competitiveness (Workshop on Materials and Measurements for Wireless Communications, J. Res. NIST 101(6), 797-802 (1996)).

In addition to revealing the existence of new, possibly useful materials, knowledge of phase equilibria relations is important because all ceramic components are processed as mixtures to achieve "compensation", i.e., a net overall zero temperature coefficient. The technical approach taken in this project emphasizes experimental determination of previously unknown ternary (or higher) oxide systems containing one or more components or compounds that exhibit useful properties as dielectric ceramics for microwave communications. Technical efforts include synthesis; structural analysis by X-ray, electron, and neutron diffraction; determination of phase relations; and characterization (via collaborative efforts) of dielectric properties. Systems investigated this year include $BaO:Fe_2O_3:TiO_2$, $SrO:TiO_2:Nb_2O_5$, $CaO:Al_2O_3:Nb_2O_5$, $SrO:Al_2O_3:Nb_2O_5$, $CaO:TiO_2:Nb_2O_5$, and $BaO:TiO_2:Ta_2O_5$.

External Collaborations:

Characterization of dielectric properties is accomplished by collaborations with NIST staff in Boulder (RF Technology Division), and with TRAK Ceramics, Inc. Productivity in this project is enhanced by interaction with the Geology Department at the University of Maryland in the form of small contracts that support undergraduate and graduate students to work as technical assistants at NIST.

Active collaborations exist with TRAK Ceramics, Trans-Tech, and Lund University.

Planned Outcomes:

Accurate, experimentally determined phase diagrams will be available that are of immediate interest to U.S. industry involved in the production of ceramics for wireless communications systems. Diagrams that include dielectric property data will indicate the chemical identities of new, potentially useful compounds as well as the compositions of equilibrium mixtures that can be processed as ceramics with controlled properties.

Accomplishments:

The crystal structure of the new compound $Ba_{11}Fe_8Ti_9O_{41}$ was determined using single-crystal and powder X-ray diffraction methods. This new phase crystallizes in the hexagonal space group *P6₃/mmc* (No 194) (a=5.7506(3)Å, c=61.413(2)Å; Z=2; ρ_{calc}=5.75 g/cm^3) and exhibits a 26-layer structure built from close-packed [O,(Ba,O)] layers with a stacking sequence *(chcchchchcchc)₂*. Octahedral sites are occupied by a mixture of Fe^{3+} and Ti^{4+}, with some preferential ordering of the Fe ions, and tetrahedral sites are occupied by Fe^{3+}. The magnetic Fe ions were observed to concentrate within four contiguous *cp* layers around z=¼ and ¾, thus confirming previous observations by high-resolution electron microscopy that this compound exhibits "natural magnetic multilayers". Unusual structural features, including cation disorder associated with unreasonably short cation-cation separations, were observed to occur within the magnetic slabs of the structure. Indexed X-ray powder diffraction reference data for polycrystalline $Ba_{11}Fe_8Ti_9O_{41}$ were prepared. Complementary structural studies of this compound using neutron and electron diffraction are in progress, along with dielectric and magnetic property measurements.

Experimental determinations of the $CaO:Al_2O_3:Nb_2O_5$ and $SrO:Al_2O_3:Nb_2O_5$ systems were carried out with the goal of discovering low-cost alternatives to $Ba_3ZnTa_2O_9$, which is currently the only material available for high-power (100 W), high-frequency (≥ 2 GHz) resonators and filters. $CaO:Al_2O_3:Nb_2O_5$ contains a single ternary compound, Ca_2AlNbO_6, which adopts a fully 1:1 ordered double-perovskite structure with a $CaTiO_3$-type distortion. Measurements of the dielectric properties of Ca_2AlNbO_6 and the compounds that occur in equilibrium with it indicated that the compound $Ca_3Nb_2O_8$ exhibited a dielectric temperature coefficient of opposite sign; synthesis and characterization of $x Ca_2AlNbO_6$:*(1-x)*$Ca_3Nb_2O_8$ mixtures confirmed the existence of a temperature-stabilized material at the composition x=0.67. This ceramic resonated at 7 GHz with a dielectric loss tangent of 10^{-4} and a permittivity of 27. In the sister system $SrO:Al_2O_3:Nb_2O_5$, two new ternary compounds were found to exist in addition to the known double-perovskite, Sr_2AlNbO_6. The new phases occur near the stoichiometries Sr_4AlNbO_6 and $Sr_6AlNb_9O_{30}$, the former exhibiting a monoclinic structure related to perovksite, the latter a tetragonal tungsten bronze type arrangement. Characterization of these compounds is in progress.

A series of $Sr_n(Nb,Ti)_nO_{3n+2}$ structures with n = 4, 4.5, 5, 6 and 7 were studied by transmission electron microscopy. These structures are composed of infinite two-dimensional slabs of the distorted perovskite structure that are "*n*" $(Ti,Nb)O_6$ octahedra thick and extend parallel to the

$\{110\}_{perovskite}$ plane. The slabs are displaced with respect to each other by the translation vector $1/2[011]_{perovskite}$. All members of the $Sr_n(Nb,Ti)_nO_{3n+2}$ series have an orthorhombic basic lattice with $\mathbf{a} \approx a_{perovskite}$ and $\mathbf{c} \approx \sqrt{2}a_{perovskite}$, while the long b-axis increases systematically with increasing n-value. The compounds with n = 4, 5, 6 and 7 were observed to undergo a commensurate→incommensurate phase transition on cooling in the temperature range 150°C to 250°C. The wave vector of the incommensurate modulation is parallel to the [100] direction of the basic orthorhombic lattice and is close but not exactly equal to $1/2\mathbf{a}^*$. The n=5 incommensurate phase further transformed at 180°C to a monoclinic structure with the space group $P112_1/b$ (#14). For the n = 4, 6 and 7 compounds, no lock-in transition was observed down to -170°C. For the compound with n=4.5, the transition from the orthorhombic to monoclinic structure $P112_1/b$ occurred on cooling at 390°C. All transitions observed in the $Sr_n(Nb,Ti)_nO_{3n+2}$ compounds were attributed to tilting of the $(Ti,Nb)O_6$ octahedra.

Four $Ca_4Nb_2O_9 = Ca[Ca_{1/3}Nb_{2/3}]O_3$ polymorphs with ABO_3 perovskite-related crystal structures were identified by HREM/TEM investigations. These polymorphs feature three different arrangments of Ca^{2+} and Nb^{5+} cations on the B-sites of the perovskite structure. In three of the polymorphs, cation ordering is combined with octahedral tilting to produce the overall crystal symmetry. Relations between the $Ca_4Nb_2O_9$ polymorphs were analyzed in terms of crystallographic groups/subgroups, separating the effects of tilting and ordering on the symmetry changes. The observed domain structure resulting from the phase transitions between different polymorphs was related to the spatial hierarchy expected from the formal symmetry considerations. Preliminary evaluation of the dielectric properties of different $Ca_4Nb_2O_9$ polymorphs at frequences above 1 GHz indicated significant variations of the temperature coefficients of the resonant frequencies. This system therefore offers the possibility of isolating the effects of structural details on dielectric properties, while the chemical composition is held constant.

Publications:

T. Siegrist, C. Svensson, T.A. Vanderah, and R.S. Roth, "Structural Study of $Ba_{11}Fe_8Ti_9O_{41}$ by X-ray Diffraction", submitted to *Solid State Sciences*.

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T.A. Vanderah, W. Wong-Ng, B.H. Toby, V.M. Browning, R.G. Geyer, R.D. Shull, and R.S. Roth, "Characterization of Ternary Compounds in the $BaO:Fe_2O_3:TiO_2$ System: $Ba_6Fe_{45}Ti_{17}O_{106}$ and $BaFe_{11}Ti_3O_{23}$", *J. Solid State Chem.* 143, 182-197 (1999).

L.A. Bendersky, T.A. Vanderah, and R.S. Roth, "Structural Study of a Group of Magnetic-Dielectric Oxides in the $BaO:TiO_2:Fe_2O_3$ System. Part I. High-Resolution Electron Microscopy", *Phil. Mag. A* 78, 1299-1328 (1998).

PROGRAM TITLE: Phase Equilibria for Ceramics and Metals

PROJECT TITLE: High-Temperature Superconductors

Principal Investigators: Winnie Wong-Ng and Lawrence P. Cook

Technical Objective:

The objective of this project is to develop phase equilibrium diagrams of high-temperature superconducting materials pertinent to the development of practical bulk conductors. These materials include bismuth-based cuprates for powder-in-tube (PIT) tapes and wires, and $YBa_2Cu_3O_7$-type systems for coated conductors rolling assisted by biaxially textured substrate/ion beam assisted deposition (RABiTS/IBAD).

Technical Description:

Two parallel technologies are currently being pursued for the development of practical bulk conductors using the high-temperature superconducting cuprates. The PIT technology, in which silver tubing is filled with superconductor powder and repeatedly rolled and heated, is the preferred method of fabrication for BiSCCO-based superconductors. The RABiTS/IBAD coated-conductor technology, in which the superconducting phase is used as a coating on a thin metallic ribbon substrate, is of interest primarily for fabrication of $YBa_2Cu_3O_7$-type superconductors. Phase diagrams are central to the successful processing of high-T_c materials by both technologies. Systems deemed most important for the rapid advancement of these technologies were selected for study.

For the BiSCCO superconductors used in the PIT approach, the stability of the 110 K (Bi,Pb)-2223 phase in the presence of silver, and as a function of oxygen pressure, was investigated. The melting temperatures and compositions of liquids in equilibrium with (Bi,Pb)-2223 under these conditions were also determined, since melting is known to play an important role in grain alignment during processing. The entry of silver from the tubing walls into the BiSCCO superconductor melts was also considered, as this can lead to thinning of the Ag tubing and chemical modification of the superconductor. In addition, the diffusion of BiSCCO components into the silver tubing can locally alter the superconductor composition at the Ag/superconductor interface, a region known to be very important for overall current transport. Quantitative studies were therefore conducted of both the solubility of Ag in BiSCCO liquids, as well as the solubility of BiSCCO oxides in Ag. An important aspect of the research is the construction of the primary phase fields, or regions of coexistence of only superconductor plus liquid, of the BiSCCO superconductors under a range of conditions similar to the processing environment. In order to efficiently transmit the highly complex, multidimensional data to users, a web page has been developed. By making the web page interactive, users can more easily incorporate selected data into their processing models.

For the RABiTS/IBAD technologies, a study was undertaken of the BaO-Nd_2O_3-CuO system under reduced oxygen pressures similar to those used in processing. Also, since most processing is done in the absence of carbonates, BaO was used instead of $BaCO_3$. This work necessitated construction of a furnace and glovebox assembly and design of a procedure for the preparation and handling of BaO, and for the annealing of samples under controlled-atmosphere conditions. Other methods used routinely in our high-T_c phase equilibrium studies include controlled atmosphere quenching, powder XRD (including the use of a specially designed controlled atmosphere X-ray cell), DTA/TGA, SEM/EDS, and melt-wicking, in which a small sample of liquid is captured for analysis by a porous MgO wick.

External Collaborations:

This project is funded in part by DoE under the Superconductivity Program for Electric Power Systems. As program participants, we collaborate with personnel of several national laboratories including ORNL, LANL, and ANL. University collaborators include New York State Unversity at Buffalo and Florida State University. NIST collaborators external to the Ceramics Division include Anthony Kearsley of the Mathematical and Computational Sciences Division.

Planned Outcomes:

The anticipated result will be determination of a set of phase equilibrium data on superconductor stabilities and primary phase fields in the BiSCCO and $RBa_2Cu_3O_7$-type systems over a range of conditions similar to those used in commercial processing. These data, by providing the basis for optimal processing, will advance high-T_c technology, and, through reductions in cost and improvements in performance, will assist high-T_c products in reaching the marketplace. Availability of competitively priced, high-performance high-T_c materials will lead to enhanced quality of life though applications such as power transmission, motor performance, magnet design, and energy storage.

Accomplishments:

(1). Melting behavior of (Bi,Pb)-2223. A five-phase volume selected for this study showed different oxide phases under annealing atmospheres of 2.2% and 100% oxygen. The melting temperature, as expected, was the highest under oxygen, and the lowest under 2.2% oxygen. The subsolidus phase relationships, melting reaction sequences, and the melt compositions as a function of temperature were all found to be different under the two different oxygen partial pressures studied. The (Bi,Pb)-2223 phase was found to be in equilibrium with liquid over a well-defined temperature range, which increased as the oxygen partial pressure decreased.

(2). Role of Ag. We have demonstrated that Ag is important not only because of its entry into BiSCCO liquids, but also because of the solubility of various oxides in solid Ag. We have obtained solubilities in Ag at the minimum melting of each of the Ag-PbO, Ag-Bi_2O_3, Ag-SrO, Ag-CaO, Ag-CuO, and Ag-(Bi,Pb)2223 systems. Preliminary results indicate that the sum of Pb, Bi, Sr, Ca, and Cu dissolving into Ag is 3-4 mole% for 1-hour experiments, and that this percentage increases slightly as the oxygen partial pressure increases from 2.2 % to 100%. This

migration of components of the superconducting phase into Ag is sufficent to change the (Pb,Bi)-2223 composition at the Ag interface during PIT processing, and could have an impact on superconducting properties.

(3). BiSCCO Web page. We have successfully constructed the first version of the Web page for displaying the results of both the subsolidus phase compatibilities and primary phase fields of the BiSCCO 2212 and (Bi,Pb)-2223 phases. This Web page (www.ctcms.nist.gov/~roosen/BSCCO) includes a general description of the research project, publication list, and interactive computations with instructions. Users can query the data with a selected starting composition, and can determine the proximity of the selected composition to primary phase fields in multidimensional space. More features will be added in the future to allow further manipulation of the data.

(4). The phase diagram of the BaO-Nd_2O_3-CuO system. The region of the diagram in the vicinity of $Ba_{2-x}Nd_{1+x}Cu_3O_{6+x}$ has been determined under a relatively reduced atmosphere of 0.1% O_2. The phases and tie-line relationships are different from those prepared in air or 100% O_2. Along the binary BaO-Cu_2O system, the reduced phase $BaCu_2O_2$ was found in addition to $BaCuO_2$. In the solid solution series $Ba_{2-x}Nd_{1+x}Cu_3O_{6+x}$, Ba was found to substitute for Nd up to $x \approx 0.6$ at 800°C, and an orthorhombic-to-tetragonal phase transition was observed at $x \approx 0.5$. The phase $Ba_{2-x}Nd_{1+x}Cu_3O_{6+x}$ occurs in equilibrium with a total of 6 phases. Under 0.1% O_2, the eutectic melting occurs at 823°C in the region bounded by $BaCu_2O_2$, Cu_2O, and $Ba_{2-x}Nd_{1+x}Cu_3O_{6+x}$. The melt contains very little Nd and is copper rich. A plot of log pO_2 vs. 1000/T for the initial eutectic melting temperatures of the Ba-Nd-Cu-O system under five different oxygen partial pressures (1.0%, 2.2%, 7.5%, 21.2% and 100% O_2) showed a linear relationship. This plot provides a basis for estimating eutectic melting temperatures over a wide range of oxygen partial pressures.

Publications:

W. Wong-Ng, L.P. Cook, W. Greenwood, and Anthony Kearsley, Effect of Ag on the Primary Phase Field of High T_c (Bi,Pb)-2223 Superconductor, submitted to J. Mater. Res., 1999.

W. Wong-Ng and L.P. Cook, Melting Equilibria of the 2223 ([Bi,Pb]-Sr-Ca-Cu) High T_c Superconductor in Oxygen, submitted to Ceramic Transactions, 1999.

W. Wong-Ng, L.P. Cook, F. Jiang, and P.V.P.S.S. Sastry, Subsolidus Phase Equilibria of the 2223 (Bi:Sr:Ca:Cu) Phase at 840 -850 C in Air, to be submitted to Physica C.

W. Wong-Ng, L.P. Cook, W. Greenwood, A. Kearsey and C. Lawrence, Primary Phase Field of the Pb-doped 2223 High T_c Superconductor in the (Bi,Pb)-Sr-Ca-Cu-O system, J. Res. Natl. Inst. Stand. Technol., **104** 277 (1999).

W. Wong-Ng, J.P. Cline, L.P. Cook and W. Greenwood, X-ray Characterization of Compounds in the SrO-PbO System, Adv. in X-ray Analy., in press.

W. Wong-Ng, L.P. Cook and W. Greenwood, Effect of P_{02} and Ag on the Phase Formation of the Pb-2223 Superconductor, J. Mater. Res. **14** (5) 1695 1998.

W. Wong-Ng, J. Dillingham, and L.P. Cook, Phase Equilibria of the $SrO\text{-}Ho_2O_3\text{-}CuO_x$ System, J. Solid State Chem., in press.

W. Wong-Ng, J.A. Kaduk , W. Greenwood and J. Dillingham, Powder X-ray Reference Patterns of $Sr_2RGaCu_2O_7$ (R=Pr, Nd, Sm, Eu, Gd, Dy, Ho, Er, Tm, Yb and Y), Res. Natl. Inst. Stand. Technol., in press.

T. Haugan, W. Wong-Ng, L.P. Cook, L. Swartzendruber, H.J. Brown and D.T. Shaw, Flux-pinning of $Bi_2Sr_2CaCu_2O_{8+}$ and $Sr_2CaAl_2O_6$ Defects, submitted to Ceramic Transactions, 1999.

PROGRAM TITLE: Phase Equilibria for Ceramics and Metals

PROJECT TITLE: Phase Equilibria Diagrams

Principal Investigators: M.A. Clevinger, P.K. Schenck, and T.A. Vanderah

Technical Objective:

The objective of this project is to maintain and develop a state-of-the-art database of critically evaluated ceramic phase equilibria data for industrial and academic customers.

Technical Description:

Technical evaluation of phase diagrams culled from the primary literature is carried out by NIST. Preparation of the evaluated diagrams for publication and dissemination is carried out at NIST by direct collaboration with personnel of the American Ceramic Society (ACerS). The ACerS personnel are primarily supported by funds raised by the Society from industry, academia, and individuals. This collaboration of more than 60 years represents an agreement with ACerS to provide evaluated phase diagrams for the ceramic industry. The phase diagrams are supplied either in printed form or in computerized versions, and are distributed through the ACerS.

External Collaborations:

American Ceramic Society Research Associates (Christina Cedeno, Nils Swanson, and Ed Farabaugh) collaborate closely with NIST staff to computerize and produce the phase diagram publications developed in this cooperative program. Drs. Robert Roth and Helen Ondik, and Mr. Howard McMurdie serve as editors or consultants for various parts of the project.

Accomplishments:

The modernization of the hardware and software for the database, which date to the mid-1980's, has been a major area of activity this year. The current HP-based system, containing well over ten thousand database entries (UNIX, HP9000 Model I40 Minicomputer, FORTRAN) and approximately two to three times as many graphical phase diagrams (Rocky Mountain Basic, vector format, stored separately on HP series 300 workstations) must be integrated into a modern, relational database hosted on a PC-based platform. The new system must be capable of electronic publishing in a variety of formats, including a Web-based version. William Andrew Publishing was selected to design, build, and maintain the new system, which is currently scheduled to be completed in fall 2000. Two substantial modernization tasks will be carried out by NIST-ACerS data center personnel: The first is upgrading of the digitization software originally written by NIST staff to re-draw diagrams culled from the primary literature in a standardized format; this software will be embedded as a utility in the new relational database.

Completion of this upgrade was given top priority this year due to failure of the obsolete HP hard drive used for the HP digitizing workstations. The software has been upgraded, ported to modern PC's, and is presently in the beta test stage. The second major modernization task is input of 2,000 commentaries and 6,955 diagrams from older volumes of the series that do not yet exist as electronic files. This work has been initiated by hiring temporary ACerS personnel and setting up additional PC-based digitization stations.

Work is nearing completion on Volume XIII of the series Phase Equilibria Diagrams. This volume, edited by R.S. Roth, will contain phase diagrams pertinent to oxide systems. Actual publication of this volume will occur upon completion of the modernization process in fall 2000. The 1999 Bibliographic Update, containing all unpublished primary literature references, was prepared this year (761 pp). A second monograph entitled "Oxides of Ti, Nb, and Ta: Electronic Ceramics I", is now in progress, and will be edited by R.S. Roth and T.A. Vanderah. Most of the systems to be included in this volume will be of major interest to the fields of dielectric, ferroelectric, and piezoelectric ceramics.

Publication:

1999 Bibliographic Update (unpublished primary literature references) ACerS, Westerville, Ohio. 761 pp.

SYNCHROTRON RADIATION CHARACTERIZATION

The availability of synchrotron radiation is resulting in major discoveries over a wide range of disciplines. The Synchrotron Radiation Program is a development and characterization effort which includes the operation of beam stations at the National Synchrotron Light Source (NSLS) at Brookhaven National Laboratory, the commissioning and operation of new beam stations at the Advanced Photon Source (APS) at Argonne National Laboratory in a collaborative arrangement called UNI CAT with the University of Illinois, Oak Ridge National Laboratory and U.O.P. Corporation, and a microstructural characterization effort in which NIST scientists, and researchers from industry, universities and other government laboratories perform state-of-the-art measurements on advanced materials.

At these facilities, a wide range of measurements is carried out. Scientific studies currently underway include microstructural characterization of ceramics and plasma-sprayed ceramic coatings, crystal perfection of a variety of basic and applied materials, the evolution of dislocation structures as a function of deformation, and the atomic-scale and the molecular-scale structures at surfaces and interfaces in polymeric, metal/semiconductor, catalytic, and other systems of technological importance.

The APS currently offers a 100 to 10,000-fold increase in brilliance compared to the best synchrotron X-ray sources of the 1980s and the early1990s. In the years to come the APS will supplant the NSLS as this nation's premier x-ray source. The APS beam lines, currently being commissioned by NIST at UNI-CAT, incorporate the newest technology which will not only enable NIST scientists to improve significantly our real-time x-ray microscopy, ultra-small-angle x-ray scattering, in situ X-ray topography and X-ray absorption fine structure (XAFS) capabilities, but will also offer opportunities for cutting-edge experiments in structural crystallography and time-resolved structural scattering, surface / interface scattering, diffuse scattering, and magnetic scattering. NIST scientists anticipate extending our present portfolio of characterization capabilities to include an even wider range of materials measurements of importance to materials scientists and to U.S. industry.

Experimental capabilities include:

- *In situ* studies of surface relaxation and phase transitions in approximate monolayer coverage in semiconductor crystals, buried interfaces, and multilayers; the brilliance at the APS will make it possible for the first time to monitor surfaces and interfaces *in situ* during MBE or CVD.

- Investigations of ceramics, coatings, and polymers; our sensitivity will be increased by a factor of 100 in ultra-small-angle x-ray scattering.

- Imaging of defects in semiconductor crystals, photonic materials, and superconducting crystals; real-time imaging will become a practical reality at the APS and resolution will reach below 1 μm.

- Structure determination from single crystals or powders; time resolved studies during melting or phase transitions will become possible.

- Diffuse x-ray scattering determination of structures and the behavior of lattice imperfections in ceramics, metals, semiconductors, and superconductors.

- Determination of magnetic structure and defects in magnetic superlattices, high-T_C superconductors, and magnetic Compton scattering; the brilliance and circularly-polarized x-ray beams will enable magnetic x-ray measurements that could never be made before.

- X-ray absorption spectroscopy in a reactive environment.

PROGRAM TITLE: Synchrotron Radiation Characterization

PROJECT TITLE: Beamline Operation and Development

Principal Investigators: Gabrielle Long, Andrew Allen, David Black, Hal Burdette, Dan Fischer, Richard Spal, and Joseph Woicik

Technical Objectives:

The major technical objective of this project is to commission and operate the five X- ray beam stations on Sectors 33 and 34 at the Advanced Photon Source (APS), at Argonne National Laboratory, together with NIST's Collaborative Access Team (CAT) partners-University of Illinois, Oak Ridge National Laboratory, and UOP Corporation-for high-resolution diffraction, USAXS, surface and interface scattering, X-ray diffraction imaging and microtomography, XAFS, diffuse scattering, X-ray microbeam diffraction and fluorescence, and coherent scattering. Other technical objectives include the successful operation of three materials science x-ray beam stations (X23A2, X23A3, and U7A) at the National Synchrotron Light Source (NSLS), at Brookhaven National Laboratory for diffraction imaging, X-ray absorption fine structure (XAFS) spectroscopy, standing-wave X-ray measurements and ultra-soft-x-ray absorption measurements. NIST is also a partner in the operation of X24A for soft X-ray standing-wave measurements of semiconductor surfaces and interfaces.

Technical Description:

The Synchrotron Beamline Operation Program involves the commissioning and operation of beam stations with our CAT partners at the APS , and the operation of beam stations at the NSLS. Currently, more than 140 scientists per year from NIST, and from industry, universities and other government laboratories, come to the NIST advanced materials characterization beamlines at the NSLS to perform state-of-the-art measurements. In the future, some of our NSLS activities will be transferred to the APS, where the parameters of the source give us unique opportunities. Other NIST facilities, which make use of the properties of the NSLS source, will remain there. The USAXS capability was moved to the APS during 1998. Its overlap with visible light scattering and pinhole small-angle cameras has been increased significantly, and thus its ability to quantify microstructures in the micrometer range (up to 8 μm) and in the nanometer range (down to 1 nm) have both been improved significantly. As one of the few SAXS instruments in the world for which a primary absolute calibration is available, the data from the NIST instrument serves an important role in setting scattering standards.

The high-resolution, monochromatic X-ray topography camera at the NSLS is the only dedicated monochromatic facility of its type in this country, and is the only instrument able to support experiments at the highest resolution. The new X-ray topography instrument, with increased sensitivity generally, and increased sensitivity to surface microstructures in particular, awaits installation at the APS during 1999.

At U7A, a refocussing mirror which produces a sub-millimeter spot has been installed. A sample manipulator and preparation/load lock chamber, which allows rapid sample entry as well as sample pre-treatment, has been installed. And finally, a focussing wavelength dispersive detection system was brought on line. This last system effectively reduces the scattered light and fluorescence backgrounds to nearly zero.

The range of scientific problems currently being addressed at the NSLS includes: microstructure evolution during hydration of cements (see, "Characterization of Cements" under Other Programs), studies of bonding and bond lengths in strained semiconductor layers, damage in sapphire windows, surface characterization of joint replacement materials, tribochemical reactions on surfaces, orientation of lubricants on hard disk magnetic media substrates, and development of new catalysts and biomaterials. The investigation of the formation of dislocation structures, which is a problem on which very little progress had been made over 50 years of effort, has enjoyed remarkable success in measuring the total line length of populations of dislocations, the presence of correlations between dislocations, relaxation of dislocation structures at room temperature in aluminum, and the presence of dipole (and possibly higher) dislocation configurations.

Accomplishments:

The new ultra-small-angle X-ray scattering (USAXS) instrument has been commissioned as part of the UNICAT facility on the 33-ID line at the Advanced Photon Source, and is now operational It offers continuously-tunable optics for anomalous USAXS, 1000 times the intensity of earlier USAXS instruments, high sensitivity and high resolution at low scattering vector, and a scattering vector range from below 0.00015 $Å^{-1}$ to above 0.5 $Å^{-1}$. Early results include USAXS from colloidal silica suspensions, and anomalous USAXS from rare-earth oxides in the presence of similarly-sized cavities in silicon nitride. The addition of side-reflection optics, in an optional configuration of this instrument, enables USAXS measurements of anisotropic as well as isotropic materials.

The instrumentation for the bending magnet beam line is complete and is awaiting the arrival of the monochromator for the bending magnet line of Sector 33 before shipment to the APS .
Procurement for Sector 34 apparatus is beginning to arrive at the APS. Radiation enclosures are complete. Kirkpatrick-Baez mirrors and Fresnel lens optics will soon be installed.

External Collaborators:

Haydn Chen and T. C. Chiang, University of Illinois, Gene Ice and Ben Larson, Oak Ridge National Laboratory, Robert Broach, UOP Corporation, H. Boukari and M. Harris, University of Maryland, G. Beaucage and D. Schaefer, U. of Cincinnati, R. Livingston, Federal Highway Administration.

Planned Outcome:

The availability of synchrotron radiation is resulting in major discoveries over a wide range of research in advanced materials science and processing. The APS offers a 100 to 10,000-fold increase in brilliance compared to the best synchrotron x-ray sources of today, and thus, in the years to come, the APS will supplant the NSLS in some areas as this nation's premier x-ray source. The new NIST facilities at the APS are extending our present portfolio of characterization capabilities to include an even wider range of advanced materials measurements of importance to materials scientists and US industry.

In the metal-forming industry, much time and money are spent perfecting dies to press sheet metal into parts. Current finite element modeling computer codes do not accurately simulate what shape a die will produce and so manufacturers use trial and error until they achieve a die that works. Underlying the finite element modeling are constitutive laws that, up to now, are based upon empirical results. To address the need for quantitative data, our *in situ* ultra-small-angle x-ray scattering during metal deformation was developed. This new capability is being used to measure the evolution of defect structures in metals as they are deformed, where these defect structures determine the mechanical properties of the metal. The new data represents a critical first step toward developing physically-based constitutive laws. With such laws in place, finite element models can be redeveloped, transforming what has been an empirical craft into a science.

Impacts:

Studies of the relationship between microstructure development in hydrating cement and the morphology of additives have been key to development of effective additives in this important material.

Fundamental measurements of dislocation formation as a function of strain in single-crystal materials are leading to physics-based constitutive laws for future redevelopment of finite-element modeling codes.

Studies of defect formation in sapphire windows enables improved assessment of the surface and subsurface integrity of these materials, and has led to improved processing protocols.

Research into the theory and measurement of bond-length distortions in strained-semiconductor alloy has led to a unifying picture of macroscopic elasticity and the microscopic distortions which arise from alloying and pseudomorphic strain.

Publications:

Four PhD dissertations were completed this year on the NIST beamlines:

I. Moulin, "Speciation of Lead, Copper, Zinc, Chromium (III) and Chromium (IV) in hydrated cement phases", Ph.D Thesis, University of Aix-Marseille III, France, 1999.

S. Kostov, "X-ray Spectroscopic Studies of Secondary Battery Materials," Ph.D Thesis, City University of New York, 1998.

Di Wei, "Synthesis, Characterization and Catalytic Properties of V-, Ti- and Cr-MCM-41 Mesoporous Molecular Sieves," Ph.D Thesis, Yale University, 1998.

M. Balasubramaniun, "Studies of ternary doped intermetallic and nanostructured materials using x-ray absorption spectroscopy," Ph.D Thesis, University of Connecticut, 1996.

NIST Publications:
D. Black, R. Polvani, K. Medicus and H. Burdette, "X-ray Topography Study of Surface Damage in Single-Crystal Sapphire," Proc. MRS Symposium R: Applications of Synchrotron Radiation to Materials Science (Boston, December 1999).

D.R. Black and G.G. Long, "X-ray Topography," invited contribution to Methods in Materials Research, A Current Protocols Publication (1999).

H. Boukari, G.G. Long and M.T. Harris, "Polydispersity during the formation and growth of Str"ber silica particles from SAXS and USAXS measurements," submitted to J. Colloid. Interf. Sci. (1999).

G. Beaucage, S. Rane, D.W. Schaefer, G.G. Long and D. Fischer, "Morphology of polyethylene-carbon black composites," J. Polym. Sci.: Polym. Phys. 37 (1999) 1105 - 1119.

R. Deslattes, E. Kessler, S. Owens, D. Black and A. Henins, "Just How Perfect Can a Perfect Crystal Be," J. Appl. Phys. D:Appl. Phys., 32 [10A] (1999) A3 - A7.

W. Dorsch, B. Steiner, M. Albrecht, H.P. Strunk, H. Wawra, and G. Wagner, "The transition from ripples to islands in strained heteroepitaxial growth under low driving forces," J. Cryst. Growth 183 [3] (1998) 305 - 310.

M. Goldman, R. Gronsky, G.G. Long and L. Pruit, "The effects of hydrogen peroxide and sterilization on the structure of ultra-high molecular-weight polyethylene," Polym. Degrad. Stabil. 62 [1] (1998) 97 - 104.

H.M. Kerch, G.G. Long, S. Krueger, A.J. Allen, R. Gerhardt and F. Cosandey, "Characterization of Porosity over Many Length Scales: Application to Colloidal Gels," J. Mater. Res., 14 (1999) 1444 - 1454.

L.E. Levine, G.G. Long and Robb Thomson, "In-situ ultra-small-angle X-ray scattering from dislocation structures in plastically-deformed single-crystal aluminum," submitted to Phys. Rev. B (1999).

G.G. Long, L.E. Levine, Robb Thomson, "In-situ observation of small-angle X- ray scattering by dislocations," submitted to J. Appl. Cryst. (1999).

G.G. Long, S. Krueger and A.J. Allen; "Multiple Small-Angle Neutron Scattering," J. Neutron Res. 7 (1999) 195 - 210.
J.J. Thomas, H.M. Jennings and A.J. Allen, "The Surface Area of Cement Paste as Measured by Neutron Scattering - Evidence for Two C-S-H Morphologies," Cement and Concrete Research 28 (1998) 897 - 905.

J.J. Thomas, H.M. Jennings and A.J. Allen; "The Surface Area of Hardened Cement Paste as Measured by Various Techniques," Concrete Science and Engineering 1 (1999) 45 - 64.

Robb Thomson, L.E. Levine, and G.G. Long, "Small-angle scattering by dislocations," Acta Cryst. A 55 (1999) 433 - 447.

J.C. Woicik, J.O. Cross, C.E. Bouldin, B. Ravel, J.G. Pellegrino, B. Steiner, S.G. Bompadre, L.B. Sorensen, K.E. Miyano, andJ.P. Kirkland, "Diffraction anomalous fine-structure study of strained Ga1-xInxAs on GaAs(001)," Phys. Rev. B-Condensed Matter 58 [8] (1998) R4215 - R4218.

Non-NIST Users of NIST facilities publications:

U. Mukai, R.E. Cohen, A. Bellare, and R.J. Albalak, "The influence of melt processing on the spatial organization of polymer chains in a crystallizable diblock copolymer of nylon and PDMS," J. Appl. Polym. Sci. 70 [10] (1998) 1985 - 1990.

R.T. Myers, R.E. Cohen, and A. Bellare, "Use of ultra-small-angle X-ray scattering to measure grain sizes of lamellar styrene-butadiene block copolymers," Macromolecule 32 [8] (1999) 2706 - 2711.

V. Promnath, A. Bellare, E.W. Merrill, M. Jasty and W.H. Harris, "Molecular rearrangements in ultra-high molecular-weight polyethylene after irradiation and long-term storage in air," Polymer 40 [9] (1999) 2215 - 2229.

PROGRAM TITLE: Synchrotron Radiation Characterization

PROJECT TITLE: Characterization of Deformation in Aluminum

Principal Investigators: Gabrielle Long, Lyle E. Levine (855), Robb Thomson (850)

Technical Objectives:

The technical objective of this program is to obtain data on plastic deformation of metals that will facilitate the introduction of lightweight materials into automobiles.

Technical Description:

The required data will be acquired, in part, through the application of ultra-small-angle X-ray scattering (USAXS) from single crystal Al. The microstructures under investigation pertain to dislocation structures where these span a wide range of sizes. The size window of the USAXS observations includes single dislocations, correlations between dislocations, dislocation dipoles, dislocation walls, and the interfaces between the walls and the nearly dislocation-free material outside them.

Over the past 48 years, many attempts have been made to use small angle scattering to study the microstructure of cold-worked metals. These attempts met with little success due to the low scattering contrast of dislocations, the strong angular dependence of the scattering, and problems associated with avoiding other, much higher contrast, processes such as accidental Bragg diffraction. In addition, the range of scattering angle where the dislocation walls are visible is outside the range of most SAS experiments. The current series of experiments are the first to map out the detailed behavior of scattering by dislocations and dislocation structures.

A collimated, monochromatic, long-wavelength (1.76 Å) X-ray beam passes through a thin aluminum single crystal, and the USAXS is measured in situ as a function of applied stress and plastic strain.

External Collaborators:

This program is the Ceramics Division, Synchrotron Radiation Characterization, portion of the "Lightweight Materials for Automotive Applications" Program that is headed by the Metallurgy Division. The very large number of external collaborators are listed in the Metallurgy Division Annual Report, 1999.

Accomplishments:

The experiments have measured the increase in dislocation density with increasing deformation, probed positional correlations between dislocations, measured the changing interface width of the dislocation walls, detected the presence of dislocation dipoles, examined the inhomogeneity of the microstructure, and measured changes in the dislocation structures during room-temperature creep.

Publications:

L.E. Levine, G.G. Long and Robb Thomson, "*In situ* ultra-small-angle X-ray scattering from dislocation structures in plastically-deformed single-crystal aluminum," submitted to Phys. Rev. B (1999).

G.G. Long, L.E. Levine, Robb Thomson, "*In situ* observation of small-angle X- ray scattering by dislocations,"submitted to J. Appl. Cryst. (1999).

PROGRAM TITLE: Synchrotron Radiation Characterization

PROJECT TITLE: Damage in Sapphire

Principal Investigators: David Black and Robert Polvani (821)

Technical Objectives:

The technical objectives of this project are to: 1) develop characterization tools to detect surface and subsurface damage, residual stresses and other crystallographic defects in single-crystal sapphire; 2) apply these techniques to observe growth related defects and stress and to characterize damage caused by fabrication or other processing procedures; and, 3) correlate these observations to predicted and observed reliability tests.

Technical Description:

The physical properties of single-crystal sapphire make it an ideal material for the windows or domes used in the IR seekers of anti-ballistic missiles. Principal among these properties are good abrasion resistance or hardness, high dynamic thermal- shock resistance and superior strength at elevated temperatures. Factors affecting the reliability of these components in-service include the presence of surface flaws, e. g. from the fabrication process or subsequent handling, crystal quality, e.g. residual stresses and/or subgrain structure from the growth process, the crystallographic orientation of the components and thermomechanical processing for property enhancement. To produce windows and domes at the lowest cost with the highest reliability, processing induced surface and subsurface damage must be identified and minimized. Residual stresses from growth or other processing procedures must be identified and minimized and thermostructural models of in-service performance must be verified.

The technical objectives of this project are being met with a series of experiments on sapphire modulus of rupture (MOR) bars, hemispheric domes and circular coupons. The bars are part of the Sapphire Statistical Characterization and Risk Reduction (SSCARR) program. This is an inter-service (Air Force, Army and Navy) program designed to meet two needs, develop an engineering database for design engineers and explore new methods to improve the bulk strength of sapphire. The sample set of MOR bars combines the effects of crystal growth method, sample fabrication technique, crystallographic orientation, and post-fabrication processing and represents all combinations currently used in antiballistic missile programs. The domes are part of the Navy antiballistic missile program. In this program, the effects of crystallographic orientation, surface finish, growth method and surface coatings on the reliability of domes is being evaluated using a supersonic wind tunnel to duplicate in-service conditions, and using a laser proof test to subject domes to thermal stresses. X-ray topography and optical microscopy, including Nomarski and polarized light, are used before and after testing to evaluate the relative importance of each different condition on reliability. Post mortem examination of failed components provides the opportunity to pin point specific causes of failure.

External Collaborators:

Fred Schmid of Crystal Systems Inc. grows high-quality sapphire, supplies samples with specific surface preparation and performs thermal treatments. Dan Harris of the Naval Air Warfare Center supplies samples and helps in the interpretation of data. Ender Savrun of Sienna Technologies provides samples and related diffraction data. Kelly Fraser of the Johns Hopkins Applied Physics laboratory performs wind tunnel testing and aids in the interpretation of data. Jim Gottlieb of Raytheon Missile Systems provides domes and related thermostructural data. Fracture data are supplied by the University of Dayton Research Institute.

Accomplishments:

X-ray topography has been used to characterize the surface of domes in a variety of diffraction conditions. Specific diffraction conditions have been identified to emphasize surface structures in the highest stress regions of the domes and to examine the fracture surfaces of failed components.Strength limiting subsurface damage has been observed using x-ray topography and correlated to subsequent fracture data. Combining topography with several optical characterization
techniques has led to a proposed inspection standard for sapphire components.

Publications:

David Black, Robert Polvani, Katherine Medicus and Harold Burdette, X-ray Topography Study of Surface Damage in Single-Crystal Sapphire," Proceedings of MRS Symposium R: Applications of Synchrotron Radiation to Materials Science, Boston, December 1999.

PROGRAM TITLE: Synchrotron Radiation Characterization

PROJECT TITLE: Development of Instrumentation for X-Ray Microtomography

Principal Investigator: Richard Spal

Technical Objective:

The technical objective is to develop X-ray microtomography of ceramics and other materials, at spatial resolutions down to 1 μm, using the NIST/UNICAT undulator beamline at the APS. The spatial resolution and field of view will be adjustable by a factor of about 4, with the field increasing from 250 μm to 1000 μm as the resolution varies from 1 μm to 4 μm. Data acquisition will take less than 1 hour, for objects smaller than the field of view. The instrument will operate with monochromatic radiation ranging from 8 keV to 40 keV. Finally, the instrument will be portable, since it must be stored outside the experimental hutch when not in use.

Technical Description:

The instrument consists of three stages-the aperture, object, and image stages-which are assembled on an optical table and receive the incident beam in the order listed. The table rests on three rigid kinematic supports, and is transported by an elevating carriage which fits between the supports. The aperture stage has orthogonal slits, a shutter, and an ion chamber.

The object stage has a rotator to turn the object about the primary axis, four translators to center the object on the primary axis and in the beam, and two rotators to orient the primary axis. During a tomographic scan, only the rotator which turns the object about the primary axis, and two translators which center the object on the primary axis, are used. Consequently, these three positioners have the highest precision: the rotator has radial and axial runout below 0.1 μm, which is achieved with a rotary air bearing; and the translators have repeatability of 0.05 μm, which is achieved with 0.05 μm resolution encoders and servo control.

The image stage has an asymmetric Bragg diffraction microscope (ABDM), and translators to position the ABDM along three axes. The ABDM uses asymmetric Bragg diffraction from a pair of flat silicon crystals to magnify the radiographic image of the object by an adjustable factor, ranging from 10 to 40 as the spatial resolution varies from 4 μm to 1 μm. The magnified x-ray image is converted by a single crystal x-ray scintillator to a visible image, which is focused by a lens without further magnification onto a 1 x 1 cm^2 CCD detector with 20 μm square pixels. This microscope is an improved version of one which was routinely used to perform microradiography at about 1 μm resolution on the NIST beamline X23A3 at the NSLS.

External Collaborators:

Haydn Chen and T. C. Chiang, University of Illinois, Gene Ice and Ben Larson, Oak Ridge National Laboratory, and Robert Broach, UOP Corporation,.

Planned Outcomes:

It is expected that the above technical objectives will be met, thereby creating a versatile, state-of-the-art instrument for microtomography, which will be applied to study nondestructively materials having inhomogeneities on a scale of 1 μm and greater.

Accomplishments:

Two key features have been implemented for the first time in an instrument for microtomography. The first feature is an air bearing on the primary rotation axis, which assures that runout will not be a significant source of error. Solid bearings generally have runouts in excess of 1 μm, which cannot be corrected easily. The second feature is an ABDM, which enables use of a scintillator with much higher detection efficiency, as mentioned above. (It should be noted that some instruments for microtomography already use a one-dimensional ABDM, which provides magnification in one direction only, but none use a two-dimensional ABDM.)

The ABDM has been improved significantly compared to its predecessor at the NSLS. For example, the earlier instrument converted x-rays directly to electrical charge in the CCD, rather than indirectly via visible photons emitted by an x-ray scintillator. The incorporation of the scintillator greatly increases the x-ray detection efficiency, and eliminates radiation damage to the CCD. Finally, procurement of the mechanical components of the instrument is nearly complete.

PROGRAM TITLE: Synchrotron Radiation Characterization

PROJECT TITLE: NIST/Dow Soft X-ray Materials Characterization

Principal Investigator: Daniel A. Fischer

Technical Objective:
The objective is to operate a unique world class facility for ultra-soft X-ray absorption spectroscopy of diverse materials important to NIST and our industrial and academic partners.

Technical Description:

The U7A materials science endstation is a materials characterization facility with unique capabilities, complete with instrumentation and analysis software. The key feature of the endstation is that it enables non-ultra-high-vacuum ultrasoft-x-ray materials characterization that reaches beyond single-crystal surfaces (i.e., traditional surface science) into the realm of catalysis, biomaterials, polymer science, data storage applications, high-Tc superconductivity and tribology.

External Collaborators:

J. Gland (U. of Michigan), Sarah Sambasivan (Dow/NSLS), W. Goodmen (Texas A&M), J. Hrbek (Brookhaven National Laboratory), T. Madey (Rutgers University, J. Rodriguez (Brookhaven National Laboratory), E. Rightor (Dow), and M. Strongin (Brookhaven National Laboratory). Our Industrial Partners this year were: Dow, Osmic, International Radiation Detectors, Princeton Gamma Tech, Intevac, National Storage Industry Consortium, IBM, Texaco, NIST Artificial Joint Consortium, Zimmer, Howmedica, UOP, and Rohn and Hass. Our University Partners were: Temple University, Cornell University, University of Michigan, University of Washington, University of California/Santa Barbara, North Carolina University, Columbia University, SUNY at Stony Brook, Rutgers University, Texas A&M and Florida State University. Our laboratory partner was: Brookhaven National Laboratory.

Planned Outcomes:

The goal is to operate this world-class facility so that soft-X-rays at the NSLS can be used in a materials analysis mode.

Accomplishments:

It is now possible to obtain previously-inaccessible in situ data on polymers and catalysts. Ultrasoft-x-ray measurements and analysis are now routinely used in polymer science, catalysis, high-Tc superconductivity, and, most recently, tribology. (See Dental and Medical Materials Program and Magnetic Materials Program in this Report.)

A. Molecular Orientation in Artificial Joint Polymers: Characterizing the Precursors of Wear with Soft X-ray Absorption:

D.A. Fischer (NIST), S. Sambassivan (NSLS), M. Shen (U. of Maryland), and S.M. Hsu (NIST).

Over half a million patients receive artificial joint replacements annually and practically all the replacements consist of a sliding pair represented by a polymer (ultra-high molecular weight polyethylene, UHMWPE) and a hard counterface (metal or ceramic). For the past 30 years UHMWPE has remained the dominant polymer in artificial joints due to its outstanding wear resistance properties. It has been recognized that wear of UHMWPE contributes to the loosening of the implants and is the main cause for the failure of long-term implants. There is a need to understand the mechanism and the surface morphology leading to wear and failure of the artificial joint. Molecular orientation in biomaterials is thought to be critical in characterizing the precursors of wear and the production of debris during the wear process. Current methods of inferring or deducing orientation are not accurate and often rely on staining and cutting specimens. In our study we used the electric field polarization dependence of soft x-ray absorption to directly determine molecular orientation in UHMWPE and for evaluating artificial joint materials. We have measured the change in molecular orientation of ultra high molecular weight polyethylene (UHMWPE) samples subjected to various wear motions and duration. Three motions were used: a unidirectional reciporcating and a cross-shear (motion to form figure-eight) motion. Our quantitative orientation measurements of the UHMWPE molecular chains using soft x-ray absorption are the first direct evidence supporting the current published wear process hypothesis. The measurements attracted a great deal of enthusiasm and interest within the NIST Orthopedic CRDA Consortium and at the Society for Biomaterials annual meeting.

B. Intevac ATP intramural project:

D.A. Fischer (NIST), S.M. Hsu (NIST), B. M. DeKoven (Intevac)

This year we have been using the chemical and surface (10 nm) sensitive soft x-ray absorption spectroscopy to probe the ZDOL hardcoat interface above the surface of magnetic media hard disks. The chemical bond specificity of the soft x-ray absorption technique enables the differentiation of the carbon in ZDOL from the hardcoat. Preservation of the integrity of the ZDOL lubricant is important for the long-term reliability of the magnetic hard disk media. The industry standard is to apply ZDOL in a dip coating process (in air) after the vacuum sputtering of the carbon hard coat to the media is complete. Recently Intevac has pioneered an alternative ZDOL coating technique utilizing vapor deposition of the ZDOL lubricant under vacuum after the hard coat deposition with no air exposure. From our results it appears that the *in situ* vapor deposition produces a chemical interaction between the lube and the hardcoat. This chemical interaction promotes the bonding and the retention of ZDOL to the hardcoat at a significantly higher level then the standard dip coating process.

C. Dow ATP intramural project:

D.A. Fischer (NIST), S. Sambassivan (Dow/NSLS), A. Kuperman (Dow)
This year we have continued infrastructure improvements to the Dow/NIST Soft X- ray Materials Characterization Facility in nitrogen fluorescence detector technology. With Dow scientists we used soft x-ray absorption to non destructively characterize propylene chemistry on silver zeolite, a non proprietary catalyst sample, in an effort to understand the nature of the active catalyst site. This year Texaco, UOP, and Rohm & Hass have become general users performing nonproprietary collaborations using the materials characterization facility.

- Direct Observation of Propylene Transformation Chemistry on and in the Pores of Silver Exchanged Faujasite Catalyst: For the first time Near-Edge Soft X-ray Absorption Spectroscopy Fine Structure (NEXAFS) electron yield (surface sensitive about 50 μm) and fluorescence yield (bulk sensitive) have been applied simultaneously to characterize the adsorbed state of propylene in the surface and the bulk of the silver exchanged faujasite (LZY-52) catalyst. This technique is non-destructive, element specific, and a direct probe of the bonding and concentration of the adsorbed species, and reactive intermediates on a highly complex zeolite catalyst. Propylene adsorption on Ag/LZY-52 faujasite at 125 K showed that a bulk adsorbed state was a weakly interacting gas-phase like species with a highly intense carbon 1s to pi* intensity which begins to desorb upon heating from 150 K to 300 K. On the other hand the propylene adsorbed on the surface forms a strongly chemisorbed intermediate with a small of carbon 1s to pi* intensity but a strong pi* intensity indicating a formation of a sigma complex which is stable up to 250 K. A very small adsorption of propylene was observed on a zeolite with similar cage structure, high Si/Al ratio and no silver loading.

- Implementation of a windowless energy dispersive SiLi solid state detector providing about 5 times better oxygen fluorescence detection sensitivity over our existing proportional counter. With the solid state detector, improved sensitivity for elements heavier then carbon i.e. N, O F (k edges), Ti, Cr, Mn, Fe Co, Ni, Cu, Zn (L edges). Tilizing this detector improvement, soft x-ray fluorescence yield NEXAFS at the metal L edge and Oxygen K edge will greatly aid our study of the electronic state of transition metal oxides in newly developed non proprietary catalysts. The major impact is to aid the synthetic chemist in producing a desired catalyst using electronic structure information derived from metal oxide NEXAFS.

- Nitrogen based chemistry: With Dow scientists the implementation of a nitrogen wavelength dispersive detection system for soft x-ray fluorescence yield NEXAFS of nitrogen intermediates in activated, inactivated and "burned" catalyst samples. The wavelength dispersive detection system has been specified, ordered and acquired and is now being tested and should significantly reduce backgrounds in nitrogen NEXAFS spectra during the characterization of reaction intermediates.

Publications:

D. J. Perettie, B. M. DeKoven, T. A. Morgan, D. A. Fischer, S. M. Hsu, F. E. Talke, H. J. Kang and C. Singh Bhatia, "The use of advanced lubricant additives to enhance the performance of the head/disk interface: the effect of surface energy and orientation," Transactions of the Society of Lubrication Engineers(1999).

D.A. Fischer, S. Sambassivan, M. Shen, and S.M. Hsu, "Wear Induced Molecular Orientation in Ultra High Molecular Weight Polyethylene (UHMWPE) Measured by Soft X-Ray Adsorption," Transactions of the Society for Biomaterials, 22 (1999) 352.

S. Sambassivan, D.A. Fischer, M. Shen, and S.M. Hsu "Effects of Wear Motion on Ultra High Molecular Weight Polyethylene (UHMWPE) Molecular Orientation," Transactions of the Society for Biomaterials 22 (1999) 194.

J. Genzer, E. Sivaniah, E. Kramer, J. Wang, H. Korner, K. Char, C. Ober, B. DeKoven, R. Bubeck, D. Fischer, S. Sambasivan, "Temperature dependence of molecular orientation on the surfaces of semi-fluorinated polymers thin films," submitted to Physical Review Letters.

J. Genzer, E. Sivaniah, E. Kramer, J. Wang, H. Korner, K. Char, C. Ober, B. DeKoven, R. Bubeck, M. Chaudhury, S. Sambasivan and D. Fischer, "The orientation of semifluorinated alkanes attached to polymers at the surface of polymer films," Submitted to Macromolecules.

Aaron M. Gabelnick, Adam T. Capitano, Sean M. Kane, John L. Gland , and Daniel A. Fischer, "Propylene Oxidation Mechanisms and Intermediates Using In-Situ Soft X- ray Fluorescence Methods on the Pt (111) Surface," Submitted to Journal of Physical Chemistry.

R. Moodenbaugh, B. Nielsen, S. Sambasivan, D. A. Fischer, T. Friessnegg, S. Aggarwal, and R. Ramesh, "Hole state density of La1-xSrxCoO3-d (0óxó0.5) across the insulator/metal phase boundary," by A. Submitted to Physical Review B.

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Jose a. Rodriguez, Tomas Jirask, Joesph Dvorak, Sharadha Sambasivan, and Daniel A. Fischer, "Reaction of NO2 with Zn and ZnO: Photoemission, XANES and Density Functional Studies of the Formation of NO3," Submitted to Journal of Physical Chemistry.

Lara Gamble, Joanna R. Long, Patrick S. Stayton, Daniel A. Fischer, Sharadha Sambasivan, David G. Castner, "Orientation of Surface Bound Proteins Studied by Near Edge X-ray Absorption Fine Structure," Submitted to Transactions of the Society for Biomaterials.

S. Sambasivan, D. A. Fischer, M. Shen, J. Tesk and S. M. Hsu, "Effects of Annealing on

UHMWPE Molecular Orientation," submitted to Transactions of the Society for Biomaterials.

U7A Facility Publications by others:

L. Gamble, J. Long, P. Stayton, and D. Castner, "Pepetide Orientation on Surfaces as Determined by Near Edge X-rayAbsorption Spectrscopy," Transactions of the Society for Biomaterials , 22 (1999) 355.
J.A. Rodriguez, S. Chaturvedi, J.C. Hanson and J.L. Brito, "Reaction of H2 and H2S with CoMoO4 and NiMoO4: TPR, XANES, Time-Resolved XRD, and Molecular-Orbital Studies" J. Phys. Chem. B, 103 (1999) 770-781.

C.I. Butoi, N.M. Mackie, J.L. Barnd, L.J. Gamble, D.G. Castner, and E.R. Fisher, "Control of Surface Film Composition with Downstream PECVD of Hexafluoropropylene Oxide," Chem Materials, 11, 862-864, 1999.

K.E. Nelson, L.S. Jung, L. Gamble, M.S. Boeckl, E. Naeemi, C.T. Campbell, S. L. Golledge, T. Sasaki, D.G. Castner, and P.S. Stayton, "Surface Characterization of Mixed Self-Assembled Monolayers Designed for Streptavidin Immobilization," submitted, Langmuir, 1998.

C.I. Butoi, N.M. Mackie, J.L. Barnd, D.G. Castner, and E.R. Fisher, "Control of Surface Film Composition with Downstream PECVD of Hexafluoropropylene Oxide," to be submitted, Chemistry of Materials, 1998.

J.A. Rodriguez, S. Chaturvedi, J.C. Hanson and J.L. Brito, "Reaction of H2 and H2S with CoMoO4 and NiMoO4: TPR, XANES, Time-Resolved XRD, and Molecular-Orbital Studies," J. Phys. Chem. B, in press (1999).

K.E. Nelson, L.S. Jung, L. Gamble, M.S. Boeckl, E. Naeemi, C.T. Campbell, S. L. Golledge, T. Sasaki, D.G. Castner, and P.S. Stayton, "Surface Characterization of Mixed Self-Assembled Monolayers Designed for Streptavidin Immobilization," submitted, Langmuir, 1998.

PROGRAM TITLE: Synchrotron Radiation Characterization

PROJECT TITLE: Regularity in Optoelectronic Materials

Principal Investigator: Bruce Steiner

Technical Objectives:

This project provides insight into crystal regularity, an essential cornerstone for the design and effective commercial realization of novel materials for the next generation of photonic and electronic devices in the U.S. This objective is achieved through high resolution synchrotron radiation diffraction imaging and its interpretation for novel photonic materials at successive stages in their incorporation into advanced devices.

Current technical target areas include blue laser materials, materials for quasi phase-matched laser frequency doublers and guided wave modulators, and materials for advanced radiation detectors. Applications for these devices include high capacity information transmission, innovative approaches to information processing, high capacity information storage, advanced displays, increased sensitivity in orientation during travel, and increased simplicity and reliability in monitoring nuclear technology. Priorities are established and research is carried out in collaboration with colleagues in industry, governmental laboratories, mission agencies, and universities.

Technical Description:

These technical objectives are achieved through the exploitation of one of the NIST MSEL beamline at the National Synchrotron Light Source at Brookhaven National Laboratory, Beamline X23A3, in conjunction with *in situ* laser optical fields. Specialized expertise in crystalline regularity associated with advanced crystals for information technology has been developed and is utiliized. High resolution diffraction imaging, guided by the experimental and interpretive expertise established through this activity, leads to fundamental information on crystalline irregularity. Central thrusts are the identification of prevalent types of irregularity, the development of an understanding of their influence on device performance, the determination of their genesis, and the achievement of their control through materials and device processing. The resulting insight provides a reliable basis for device design, performance optimization, and economical production of novel devices for the next generation of information processing technology.

Activity currently includes gallium nitride for blue lasers and information displays, lithium niobate frequency doublers and guided wave modulators for fiber optic gyroscopes for increasingly precise position sensors, layered systems for flat panel displays, and.mercuric iodide grown in microgravity and on the ground for optimized low noise, room temperature radiation detectors for unattended nuclear monitoring.

External Collaborations:

Current work involves: Norman Sanford and Richard Mirin, of the Optoelectronics Division of the NIST Electronics and Electrical Engineering Laboratory, which produces and characterizes optoelectronic devices; Professor Venkatraman Gopalan of the Pennsylvania State University, who studies the polling of ferroelectric materials; Gisèle Foulon and Dieter Jundt of Crystal Technology, Inc., which produces lithium niobate for these devices; William Burns, formerly of the Naval Research Laboratory, with whom we are working on the scientific basis for frequency doubler technology; Joseph Pellegrino of the Semiconductor Electronics Division, also of the NIST Electronics and Electrical Engineering Laboratory, which produces and studies innovative III-V optoelectronics devices; and Lodewijk van den Berg of Constellation Technology, Inc. Dr van den Berg is developing mercuric iodide detectors for high energy radiation as a follow up to a Department of Energy program in nuclear sensors and NASA microgravity crystal growth programs. His collaboration is valuable not only because of his commercial perspective but also because of his roll as Principal Investigator for both space flights involved and his participation as the scientist who grew the first successful crystals himself in microgravity as mission specialist on board Spacelab III.

Planned Outcomes:

A primary current target is the development of efficient, durable blue laser materials for information displays and high density information storage and transmission systems. This technology is approaching commercial realization, with keen competition between Japan and the U.S.

A closely related target is an understanding of defect structure in wafer bonded systems, which promise to provide inexpensive and highly efficient electrooptic devices for flat panel displays with promise of wide commercial application, with intense international competition.

Another primary target is modification of the lithium niobate defect structure for enhanced high capacity frequency doublers. The fabrication of high frequency doublers for lasers supports greater U.S. competitiveness in the production of high frequency optical sources for increased capacity information processing. Closely related targets are useful understanding of the evolution of strain during growth of lithium niobate crystals for fiber optic position sensors as well as for wavelength division multiplexing supporting enhanced capacity in fiber optic communications, and effective reduction in the removal of wafer material in cutting and polishing in order to achieve increased flatness for advanced photonics. With the information provided, growers of highly uniform lithium niobate single crystals will be able to make knowledgeable, economical trade-offs between crystal perfection and performance. One result is that the establishment of an destructive subgrain structure can now be prevented when it is cost effective to do so.

A continuing target is insight into the crystallographic sources of the enhanced performance of low noise, room temperature, high energy radiation detectors made from mercuric iodide crystals grown in microgravity and its application to superior mercuric iodide grown on the ground.

Accomplishments:

The native defect structure in gallium nitride, both in bulk and in overgrown layers, has been examined, providing a foundation for more successful commercial production of these important and highly competitive materials.

The formation of defects in several promising types of wafer bonded systems has been studied, starting the establishment of a firm foundation for the commercial production of these important high technology materials.

The principal sources of the high frequency roll-off in lithium niobate frequency doublers have been identified and interpreted in collaboration with the crystal grower, university collaborators, and those in the private sector who are preparing to commercialize this technology.

Improved processes for enhancement of performance of low-noise, room-temperature, high-energy radiation detectors made from mercuric iodide have been supported.

Publications:

Bruce Steiner, Lodewijk van den Berg, and Uri Laor, *"Enhancement of Mercuric Iodide Detector Performance through Crystal Growth in Microgravity: the Roles of Lattice Order"*, MRS Symp.**487** (Room-Temperature Rad. Det. Appl.) 345-350 (1998).

J.C. Woicik, J.O. Cross, C.E. Bouldin, B. Ravel, J.G. Pellegrino, B. Steiner, S.G. Bompadre, L.B. Sorensen, K.E. Miyano, and J.P. Kirkland, "*Diffraction anomalous fine structure study of strained $Ga_{1-x}In_xAs$ on GaAs(001).*, Phys. Rev. *in press* (1998)

Bruce Steiner, Lodewijk van den Berg, and Uri Laor, "Gravitational Effects on Mercuric Iodide Crystal Growth," MRS Symp. (Mat. Space - Sci., Tech., and Expl). (1998)

PROGRAM TITLE: Synchrotron Radiation Characterization

PROJECT TITLE: Semiconductor Materials Evaluation

Principal Investigator: Joseph C. Woicik

Technical Objective:

The technical objective is to develop and utilize synchrotron based measurement techniques for the characterization and study of novel semiconductor layered device structures fabricated by advanced growth techniques such as molecular beam epitaxy (MBE) and chemical vapor deposition (CVD).

Work has also been initiated to develop a direct experimental method by which spatially resolved valence-electronic structure of crystalline solids and films can be determined.

Technical Description:

This year we have extended our studies of bond-length distortions and elasticity to monolayer films of InGaAs alloys grown on GaAs substrates. Our experimental X-ray standing wave measurements of the In layer spacing relative to the GaAs substrate are in excellent agreement with an atomistic theoretical calculation of the interfacial structure. Other unique layered structures are also being studied. We are currently performing high-resolution EXAFS measurements to understand the strain relief of InAs quantum dots, and we have used the short-range order sensitivity of polarization-dependent EXAFS to demonstrate that alloy ordering occurs in AlGaN films grown on sapphire. Additionally, we are performing high-resolution X-ray diffraction measurements to determine accurately the strain state of extremely thin and highly strained GeSi alloy films grown on Si, and polarization-dependent EXAFS studies are being conducted to determine the bonding and geometric structure of epitaxial Gd_2O_3 films grown on GaAs by electron-beam evaporation.

Work has also continued on the development of a new X-ray technique for the study of electronic structure. The method is a further development of the X-ray standing wave technique because it relies on the spatial modulation of the electric field intensity inside a crystal that is produced when an incident and Bragg reflected X-ray beam are superposed. By combining high-resolution valence-electron spectroscopy with this form of X-ray diffraction, spatially resolved electronic structure should become a practical reality. This possibility arises because under the Bragg condition the maxima and minima of the electric field intensity can be aligned precisely with the different crystallographic planes of a crystal. In contrast, the electric field intensity utilized in standard photoemission measurements has no spatial variation at all.

External Collaborators:

J.G. Pellegrino (EEEL, NIST) III-V strained-layer thin-film material grown on GaAs; C.A. King (Lucent Technologies, Bell Laboratories) IV-IV strained-layer material grown on Si; M. Hong (Lucent Technologies, Bell Laboratories) Gd2O3 epitaxial layers on GaAs substrates; S. Fafard (National Research Council of Canada) InAs quantum dots on GaAs; P. Pianetta (Stanford), L. Berman (NSLS), and D. Heskett (U. of Rhode Island) two-beam X-ray diffraction experiments of valence electronic structure; Z.X. Shen (Stanford University) manganites, cuprates, and high-Tc materials; and T. Moustakas and K. Ludwig (Boston University) AlGaN ordered alloy project.

Planned Outcomes:

A unifying description of atomic structure and elastic response in ultra-thin (monolayer) films and alloy heterostructures. In some cases, this information may lead to an understanding of unique surface passivation behavior.

The development of a new and direct method for the investigation of atomic bonding in crystalline solids and films.

Accomplishments:

The problem of local geometric structure in monolayer alloy films and heterostructures has been solved.

In addition to the possibility of creating a new X-ray analytical technique for measuring valence electronic structure, our measurements of valence-electron photoemission under the condition of strong x-ray Bragg reflection has led to numerous and interesting x-ray physics contributions which will shortly be published in Physical Review Letters.

First, it was unexpected that the emission pattern from crystalline Ge valence electrons would so closely mirror the emission pattern from the tightly bound Ge core electrons. By performing similar measurements on Cu, where the valence electrons are even more delocalized, we onfirmed that this is in fact a general phenomenon for our photon energy range.

From these experiments, we concluded that our original assumption, that the measurement would be sensitive to the spatial extent of the valence wave function, was too simple. We have now explained this behavior by examining the basic physics of the photoemission process. For X-rays on the order of a few keV, the regions of bonding charge which are smoothly varying; i.e., those between the atomic nuclei where the nuclear potential is small, are transparent to the X-rays, and only the valence density in the localized region around the atomic cores contributes to the photocurrent.

Second, we have demonstrated that the technique is directly sensitive to the valence charge asymmetry of the atomic bond in heteropolar crystals; i.e., crystals which have different atoms on their atomic planes. By measuring the centroid of valence emission from a polar GaAs crystal, we

have quantitatively determined the Ga-As bond polarity. The unique combination of these two results should produce unambiguous information on the planarly resolved electronic structure for crystals with more than one type of atom.

Publications:

J.C. Woicik, E.J. Nelson, and P. Pianetta, "Direct measurement of valence-charge asymmetry by x-ray standing waves," to be published, Phys. Rev. Lett.

J.A. Gupta, S.P. Watkins, E.D. Crozier, J.C. Woicik, D.A. Harrison, D.T. Jiang, I.J. Pickering, and B.A. Karlin, "Layer perfection in ultrathin InAs quantum wells in GaAs(001)," to be published, Phys. Rev. B.

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OTHER

Several important projects in the Ceramics Division are unique and are not constituent parts of "Programs." These projects are highly visible and have significant broad impact in several application areas but generally involve a commitment of personnel and resources less than that considered to be a program. The Ceramics Division relies on these projects for enhanced technology transfer and for more effective delivery of the results of the research programs to the technical community.

PROGRAM TITLE: Other

PROJECT TITLE: Characterization of Cements

Principal Investigators: Andrew J. Allen

Technical Objectives:

The objectives of this research are to (1) characterize microstructure evolution during hydration in cements, (2) determine what aspects of the microstructure relate most directly to performance, (3) characterize microstructure degradation due to environmental effects, and (4) probe the effects of additions of silica fume, fly ash, and other additives that may lead to superior performance.

Technical Description:

This project makes use of small-angle neutron scattering (SANS) and ultra-small-angle x-ray scattering (USAXS) to characterize microstructural evolution during the hydration of cements, as a function of environmental effects and additives, as it affects highway infrastructural concretes. The program has previously explored the effects on cement hydration of silica fume (SF), and is now focussed on the effects of coal fly ash (CFA), a major coal-combustion by-product resulting from electrical power generation. Like SF, CFA is increasingly being used as a relatively inexpensive additive intended to enhance cement and concrete durability. The effects on long-term cement hydration of the two basic generic types of CFA, F and C, are being studied in a succession of SANS experiments that are revealing differences in microstructure development throughout the size range for the two types. In parallel, a combination of more fundamental SANS and USAXS studies of cement hydration are exploring the formation of the different types of the main strength-developing calcium-silicate-hydrate (C-S-H) phase as hydration proceeds.

External Collaborations:

R.A. Livingston, Federal Highway Administration, McLean monitors this program and is involved in interpretation of the SANS and USAXS measurements. J.J. Thomas and H.M. Jennings, Northwestern University, collaborate with the Ceramics Division on surface area and C-S-H gel characterization in hydrating cements utilizing SANS as the primary technique.

Planned Outcome:

These studies will enable a quantitative assessment of how the microstructures of hydrating cement systems can be controlled, by the hydration conditions and by the use of cement additives. The studies have already quantified the relationship between differences in silica fume morphology and the variable effectiveness of silica fume additives in forming cements and concretes of improved strength and durability. Present work is focussed on similar objectives for coal fly ash additives and on providing a more fundamental understanding of the mechanisms underlying the formation of the C-S-H gel.

Accomplishments:

SANS studies have continued to quantify the microstructural effects of CFA additives on cement microstructure development during hydration. A series of experiments are being carried out on a set of Portland cement (PC) / CFA blends, designed to investigate the effects on microstructural evolution during hydration at two different water-to-solids mass ratios (0.4 and 0.5), of adding varying amounts of the two main generic CFA types, C and F. In addition to the SANS studies, a compositional analysis has been made of the two CFA types as well as the PC. Differences in the blends using types C and F are manifest even at the sample mixing stage and become more striking as hydration progresses. USAXS experiments on the fly ashes themselves, both as powders and suspensions, have established little morphological difference between C and F fly ashes over the nanometer to micrometer scale range. This contrasts with the case found in the earlier study of silica fume additives in cement. Instead, large compositional differences between C and F appear to be responsible for the different microstructural evolution. Both CFA types are pozzolanic additives rather than self-activating, i.e., they become involved in the hydration reactions once these are underway and the pH becomes sufficiently high, but they do not initiate the hydration reactions just by being in contact with water themselves. However, CFA type C contains significantly more CaO and less Al_2O_3 than type F. With reference to the Ca–Si–Al ternary phase diagram, this means that PC blends incorporating type C can more readily become self-activating on contact with water than those incorporating type F. Indeed, most of the differences in microstructural evolution between type C and type F CFA/PC blends can be explained by significantly greater reactivity in the blends with type C. The implications of these results for the long-term durability of infrastructural cements and concretes incorporating CFA are being considered as the study is extended out to more than one year in real-time hydration.

Our SANS and USAXS studies of the fundamental nature of C-S-H gel in hydrating cement have focussed on determining an unambiguous phase composition and density of the C-S-H gel under various conditions. While previous H_2O/D_2O contrast variation SANS studies have enabled a selection to be made among arious C-S-H models presented in the literature, it has become clear that the literature data for density and phase for any one of these models are somewhat uncertain. In particular the water content of C-S-H is difficult to define if the water component is assumed to have a density close to 1 g cm^{-3}. Because all of the bound H in C-S-H exchanges for D in H_2O/D_2O contrast experiments, it is not possible to determine the phase and density absolutely (as opposed to selecting among literature models). There is a corresponding uncertainty in absolute measurements of C-S-H surface area, long considered an important parameter controlling cement rheology. Ultimaterly, these issues can be addressed in SANS contrast experiments using a pore medium such as CH_3OH/CD_3OH, which will not involve the C-S-H exchanging H for D. Meanwhile, it has been possible to address an associated issue: the major disagreement in the literature between measurements of cement surface area by SANS and by SAXS. By a series of carefully calibrated experiments using our new USAXS facility at the Advanced Photon Source, it has been possible to reconcile the values obtained by the two methods. These studies are continuing, aimed at obtaining unambiguous C-S-H phase, density and surface area information that can be used with other data to determine the water content and mobility in C-S-H as a function of cement content and hydration conditions.

Publications:

J.J. Thomas, H.M. Jennings and A.J. Allen; "The Surface Area of Hardened Cement Paste as Measured by Various Techniques," Concrete Science and Engineering (invited review paper), **1** 45-64 (1999).

PROGRAM TITLE: Other

PROJECT TITLE: Development of the Ceramics WebBook

Principal Investigator: Edwin F. Begley

Technical Objective:

The objective of this project is to develop the NIST Ceramics WebBook.

Technical Description:

The international success of the World Wide Web precipitated the vision of the NIST Ceramics WebBook to provide industry and the general public with efficient and ready access to Ceramics Division reference databases, topical data sets, data guides and advisories, and tools as well as other resources related to advanced ceramic materials.

External Collaborations:

During fiscal year 1996, the Systems Integration for Manufacturing Applications Program (SIMA) funded initial development of WebHTS, the World Wide Web version of the NIST High Temperature Superconducting (HTS) Materials Database. This task was designed to address on-line access to standard reference data which is a key SIMA program area for testbeds and technology transfer. In fiscal year 1997, renewed SIMA funding was used to complete WebHTS and to expand the testbed to include demonstrations of electronic collaboration and, also, the transfer of different types of technical information. In fiscal year 1998, SIMA funding was used to port the NIST Structural Ceramics Database (WebSCD) to the World Wide Web and to initiate the development of the NIST Ceramics WebBook. The Characterization of Fracture Origins in Advanced Ceramic Materials WebBook site was developed in collaboration with the United States Army Research Laboratory. During fiscal year 1999, WebHTS was updated to Version 2.0 and a multimedia glossary of terms for phase equilibria diagrams was added to the WebBook.

Planned Outcome:

The outcome of this project is the development of a World Wide Web site that will serve as an effective means of disseminating Ceramics Division reference databases, topical data sets, data guides and advisories, and tools as well as other resources related to advanced ceramic materials.

Accomplishments:

In 1996, the Property Data Summaries collection was placed on the Web and is continually updated. In 1997, the NIST High Temperature Superconducting Materials Database was ported to the Web (WebHTS). In 1998, the NIST Ceramics WebBook was added to the Ceramics Division website and the NIST Structural Ceramics Database was ported to the Web (WebSCD).

In addition, in 1998 the Guide to Materials Data Centers and Sources was added to the Ceramics WebBook as well as a website on the Characterization of Fracture Origins in Advanced Ceramic Materials and downloadable software entitled the "VAMAS Classification System for Advanced Technical Ceramics Evaluation/Demonstration Software." Links to external (non-NIST) tools and data collections were also added to the WebBook in 1998. In fiscal year 1999, WebHTS was updated to Version 2.0 and a multimedia glossary of terms for phase equilibria diagrams was added to the WebBook.

Outputs:

E. F. Begley, Web site of the NIST Ceramics Division, 1997, http://www.ceramics.nist.gov/.

E.F. Begley and R.G. Munro, Web site of the NIST High Temperature Superconducting Materials Database, 1997, WebHTS at http://www.ceramics.nist.gov/srd/hts/htsquery.htm.

E.F. Begley, Web site of the NIST Ceramics WebBook, 1998, http://www.ceramics.nist.gov/webbook/webbook.htm.

G. Quinn, J. Swab, E.F. Begley,WebBook site on Characterization of Fracture Origins in Advanced Ceramic Materials,1998, http://www.ceramics.nist.gov/webbook/fracture/fracture.htm.

E.F. Begley, S.J. Dapkunas, J. Harris, WebBook site Guide to Materials Data Centers and Sources, 1998, http://www.ceramics.nist.gov/srd/guide/guide.htm.

E.F. Begley and R.G. Munro, Web site of the NIST Structural Ceramics Database, 1998, WebSCD at http://www.ceramics.nist.gov/srd/scd/scdquery.htm.

R. G. Munro, E. F. Begley,Web site of the NIST Property Data Summaries for Advanced Materials, http://www.ceramics.nist.gov/srd/summary/advmatdb.htm.

E. F. Begley and R.G. Munro, The NIST WWW High Temperature Superconducting Materials Database (WebHTS Version 2.0), 1999, http://www.ceramics.nist.gov/srd/hts/htsquery.htm

PROGRAM TITLE: Other

PROJECT TITLE: Evaluated Materials Property Data

Principal Investigator: Ronald G. Munro

Technical Objective:

The objective of this project is to develop and promote the scientific basis for data evaluation and its practical application to materials property databases to enhance the quality and reliability of materials property data for advanced ceramics.

Technical Description:

The most persistent concern regarding the use of materials property data in industry is the reliability of the data. The lack of reliable data can result in significant losses of resources and untimely production failures. However, few design engineers and materials researchers have the resources to explore the full depth and range of publications that have been issued on a given material, and even fewer have the opportunity to assess the relevant reports fully. Consequently, there is a considerable need for the establishment of systems of evaluated property data.

The process by which data become acknowledged as reliable is often termed data evaluation. In this project, there are four distinguishable stages of data evaluation: (I) data collection from selected sources, (II) application of basic evaluation criteria, (III) relational analysis, and (IV) modeling. Useful results are derived from each stage of the evaluation process.

Stages III and IV are considered advanced data evaluation stages. In these stages, the view taken in the present project is that a material may be fully represented by its collection of measurable properties and characteristics. Experimentally, few materials are ever studied in this context. Commonly, one property measurement is made in isolation from other property measurements, and each study pertains only to the specific batch of material used in the study. In the present project, a comprehensive collection of physical, thermal, and mechanical property measurements is compiled for one nominal material specification. Subsequently, the collection is analyzed with respect to chemical composition, density, grain size, and other characteristics as needed. When sufficient constraints on these characteristics have been identified such that the property values are observed to be consistently reproducible in independent studies, then the corresponding subset of data is refined into a selfconsistent collection of property values. Theoretical and empirical property relations and statistical correlations are used as needed and warranted by the refinement.

Data assessed by each of the four stages of evaluation are collected in evaluated databases and made publicly available *via* both the NIST Standard Reference Data Program and the Ceramics

Division's website. A data quality indicator, called the data evaluation level, is provided with each data set to indicate the extent of assessment that has been applied to the data.

Planned Outcomes:

Data evaluation methodologies, including the use of data quality indicators and specific assessment procedures, will be established and applied to the development and maintenance of the Structural Ceramics Database, the High Temperature Superconductors Database, the Ceramics Coatings Database, and the NIST Property Data Summaries.

Accomplishments:

The advanced data evaluation methodology has been applied to a TiB_2. This material is well known for the relatively high values of its melting point, hardness, strength to density ratio, and wear resistance. The physical, mechanical, and thermal properties of polycrystalline TiB_2 were examined with an emphasis on the significant dependence of the properties on the density and grain size of the material specimens. Using trend analysis, property relations, and interpolation methods, a comprehensive set of well defined property values was determined for a single specification of TiB2; *viz.*, mass fraction of TiB_2 ≥95 % with a density of (4.5±0.1) g/cm^3 and a grain size of (9±1) μm.

An extensive collection of data on the fracture toughness (K_{Ic}) and strength (σ_f) of brittle materials has been used to examine the relation between the mean measured values of K_{Ic} and σ_f. Within this collection of data, it has been observed empirically that K_{Ic} is frequently linearly related to σ_f when values are compared under conditions of either constant grain size (g) or constant density (ρ). Assuming that the most significant material parameters are g and ρ, the general fracture mechanics relation among K_{Ic}, σ_f, and the critical flaw size, c_0, has been used to derive a general expression for $(\partial K_{Ic}/\partial\sigma_f)_x$ in which the subscript, x, indicates whether the condition of constant grain size, $x = g$, or constant density, $x = \rho$, applies. In general, $(\partial K_{Ic}/\partial\sigma_f)_g$ is not the same as $(\partial K_{Ic}/\partial\sigma_f)_\rho$. Imposing the empirical condition, $(\partial K_{Ic}/\partial\sigma)_x = \lambda_x$, where λ_x is a constant, a relation between strength and flaw size has been derived. For the observed conditions, the analysis indicates that the square root of the flaw size should vary as the reciprocal of the observed fracture strength.

Publications:

R. G. Munro and H. Chen, "Data Evaluation Methodology for High Temperature Superconductors," ASTM STP 1311, pp. 198-210 (1997).

R. G. Munro, "Evaluated Material Properties for a Sintered -Al_2O_3," Journal of the American Ceramic Society, Vol. 80 (8), 1919-1928 (1997).

R. G. Munro, "Material Properties of a Sintered -SiC," Journal of Physical and Chemical Reference Data, Vol. 26, No. 5, pp. 1195-1203 (1997).

R. G. Munro, S. W. Freiman, and T. L. Baker, *Fracture Toughness Data for Brittle Materials*, NISTIR 6153 (National Institute of Standards and Technology, 1998).

Other Outputs:

R. G. Munro and E. F. Begley, SRD Database Number 62: *High Temperature Superconductors, Version 2*, NIST Standard Reference Materials Program (1997).

R. G. Munro and E. F. Begley, SRD Database Number 30: *Structural Ceramics, Version 3*, NIST Standard Reference Materials Program (1998).

R. G. Munro, NIST Property Data Summaries for Advanced Materials: Al_2O_3, 1998, NIST Ceramics WebBook, http://www.ceramics.nist.gov.

R. G. Munro, NIST Property Data Summaries for Advanced Materials: *SiC*, 1998, NIST Ceramics WebBook, http://www.ceramics.nist.gov.

R. G. Munro, NIST Property Data Summaries for Advanced Materials: *Fracture Data for Brittle Materials*, 1998, NIST Ceramics WebBook, http://www.ceramics.nist.gov.

R. G. Munro and S. W. Freiman, "Correlation of Fracture Toughness and Strength," Journal of the American Ceramic Society, Vol. 82, pp. 2246-2248 (1999).

PROGRAM TITLE: Other

PROJECT TITLE: SRMs for Powder Diffraction

Principal Investigators: James P. Cline, Nicholas Armstrong, Richard D. Deslattes (842) and Jean-Louis Staudenmann (842)

Technical Objective:

The objective of this project is to develop NIST Standard Reference Materials (SRMs) to enhance the measurement capabilities of the materials science community.

Technical Description:

NIST powder diffraction SRMs are developed for the determination of: 1) the d-spacing or line position, 2) instrumental and sample contributions to the shape of reflection profiles, and 3) line intensity as a function of position, or instrument response. Additional powder diffraction SRMs are designed for quantitative analysis for use with the internal standard method.

We are presently pursuing a new generation of line position SRMs which will be certified via a robust linkage to the iodine stabilized HeNe laser length standard. This project has involved the construction of a diffractometer capable of measurement accuracy to the parts per million range. The machine has several unique features: a dual mirror optic that results in a homogeneous, parallel incident beam of high flux from a laboratory source, and an encoded goniometer capable of achieving sub-arcsecond accuracy, and symmetric scanning about the zero angle. These features permit measurements, which use the emission spectra of copper as the linkage to the SI, to be free from penetration and centration errors of the sample, and from zero errors of the goniometer. Data are analyzed with the *Fundamental Parameters Approach* wherein all contributions to the form of the data are explicitly modeled. We have obtained constant lattice parameter values regardless of which diffraction profile is evaluated, indicating both correct instrument performance and proper modeling of the observations.

This capability is being applied to the renewal of SRMs from the first three of the aforementioned categories: The feed stock for the primary line position SRM, SRM 640c (silicon powder) has been prepared from a dedicated production run of intrinsic material grown by the float zone method. After characterization, these boules of silicon were crushed and jet milled to a powder with a mean size of approximately 4.5 μm. Lastly, the feed stock was annealed at 1000 °C for two hours under gettered argon to reduce micro-strain induced profile broadening. The feed stock of SRM 660a (LaB_6 powder) was prepared commercially, via a proprietary process, to display a minimum of particle size and micro-strain induced profile broadening; it is a considerable improvement over that used for SRM 660 which displayed a slight degree of micro-strain induced broadening. This microstructural character, its certified lattice parameter, and the evenly spaced, high intensity diffraction lines, render it ideal for determination of the instrumental contribution to the observed profile shape via both whole pattern, Rietveld, and profile fitting techniques. The sintered alumina plates used for SRM 1976a are from the same source as those of SRM 1976,

thus, the lattice parameter certified for SRM 1976a will be retroactive to units of SRM 1976. However, the units of SRM 1976a will be individually certified for texture using spherical harmonics as part of a Rietveld analysis.

The observed diffraction profile from a diffractometer consists of the convolution of the specimen profile and instrument profile, with the superimposition of statistical noise and background level. Furthermore, specimen profile itself can be considered in terms of a convolution of the profiles due to the effect of crystallite size and that due to micro-strain. Although there exist several methods of deconvoluting the specimen profile from the experimental data they often require specific assumptions concerning the functional form of the size and strain profiles; otherwise, the solutions may be ill-conditioned. We solve this problem with the application the Maximum Entropy method (MaxEnt). This approach incorporates *a priori* information about the instrument profile and noise distribution as constraints, and determines the solution which maximizes the entropy with respect to said constraints. Our research is concentrating on developing a generalized MaxEnt/Bayesian method which will not only determine the specimen profile but also determine the nature of the size and strain contributions to it. Concurrent with this research is the development of SRM(s) which will address the issues of particle size and micro-strain induced profile broadening.

SRMs are also being characterized for use in quantitative analysis by powder diffraction methods of special interest is the effect of the disordered surface layer, caused by relaxation and unsatisfied bonds, that must accompany any boundary of a crystalline material. Such a boundary layer will not diffract in a manner analogous to the bulk and can be considered amorphous. In a finely divided solid, a layer of 1 or 2 crystallographic units in thickness can amount to several percent of the total mass. To perform an accurate quantitative analysis which includes the amorphous content, a standard of known phase purity must be used. Thus, a major focus of the work in this area has been the development of a measurement and certification method for the amorphous content of SRM 676, a non-orienting alumina powder which is presently certified with respect to lattice parameters and eight relative intensity values.

External Collaborations:

Robert B. Von Dreele (Los Alamos National Laboratory), Walter Kalceff and Robert W. Cheary (University of Technology, Sydney)

Planned Outcomes:

Certification of a new generation of line position SRMs with roughly an order of magnitude improvement in certainty of the certified lattice parameters will be completed with the new diffraction equipment. The MaxEnt/Baysian approach to profile deconvolution and analysis of particle size/micro-strain induced profile broadening will be established. The certification of amorphous content in SRM 676 will be measured to an improved level of accuracy.

Accomplishments:

A powder diffractometer capable of lattice parameter measurements to the parts per million range has been constructed.

The amorphous content of SRM 676, alumina powder, has been determined to within a few tenths of a percent.

The experimental approach is based on the comparison of the phase abundance of two phase mixtures determined from the preparation procedure using an analytical balance, which includes the amorphous component, to that determined from the diffraction data, which does not. Specimens consisted of 50-50 mixtures of SRM 676 and silicon powder, the latter material having been obtained from crushed and jet milled single crystal, electronic grade boules. This microstructure allowed for the assumption that all amorphous material in the silicon powder was confined to a surface layer on the particles, and that the thickness of the layer was constant with respect to particle size. Thus, by systematically varying the surface area of the silicon powder, we could model its effect on the data. However, prerequisite to the success of this method was an unbiased measurement method. Potential for bias was judged from the plausibility of the refined results obtained from a number of powder diffraction methods. Data were collected via time-of-flight, TOF, and constant wavelength, CW, neutron powder diffraction, and synchrotron and conventional x-ray powder diffraction. Analysis of the refinements indicated that the TOF data were the least biased, and thus the amorphous content of the alumina was credibly determined.

SRM 674a consists of a set of five powders: α-Al2O3, ZnO, TiO2 (rutile), Cr2O3, and CeO2, which range in x-ray mass attenuation coefficients from 126 cm^{-1} to 2203 cm^{-1} (Cu $K\alpha_1$). The materials available with this SRM permit the minimization of absorption contrast between the standard and the specimen. SRMs 1878a (α-quartz) and 1879a (cristobalite) were certified with respect to amorphous content for analysis of silica containing materials in accordance with health and safety regulations. Quantitative analysis of the silicon nitride system can be performed with SRM 656 which consists of two powders, one high in α content while the other is high in β. They are certified with respect to α / β ratio and amorphous content.

The Maximum Entropy Method has been applied to the deconvolution of the x-ray diffraction line profiles for the determination of sample induced profile broadening.

The effect of equipment optics on the observed position of profile maxima has been characterized and evaluated with a *Fundamental Parameters Approach.*

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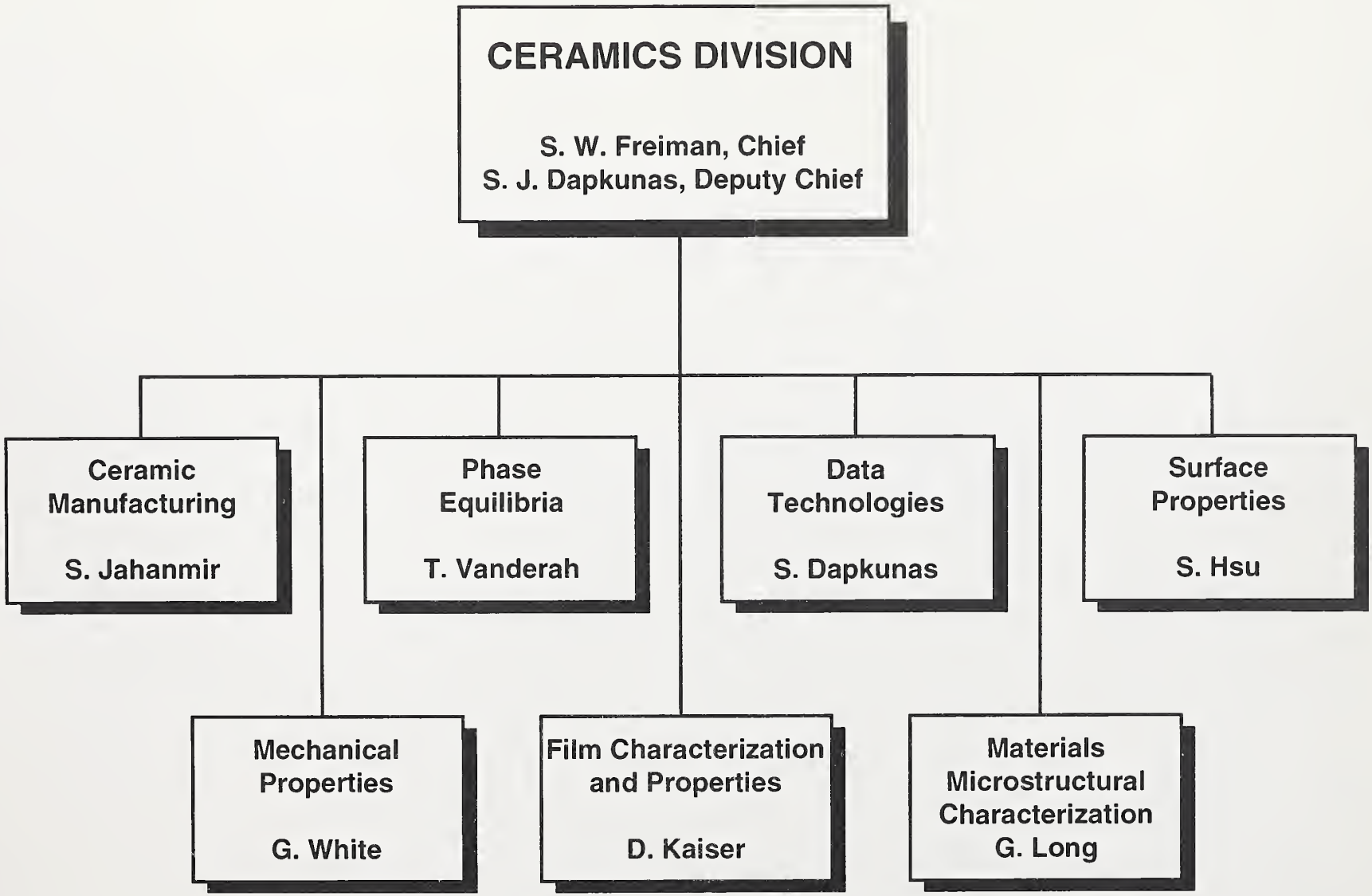
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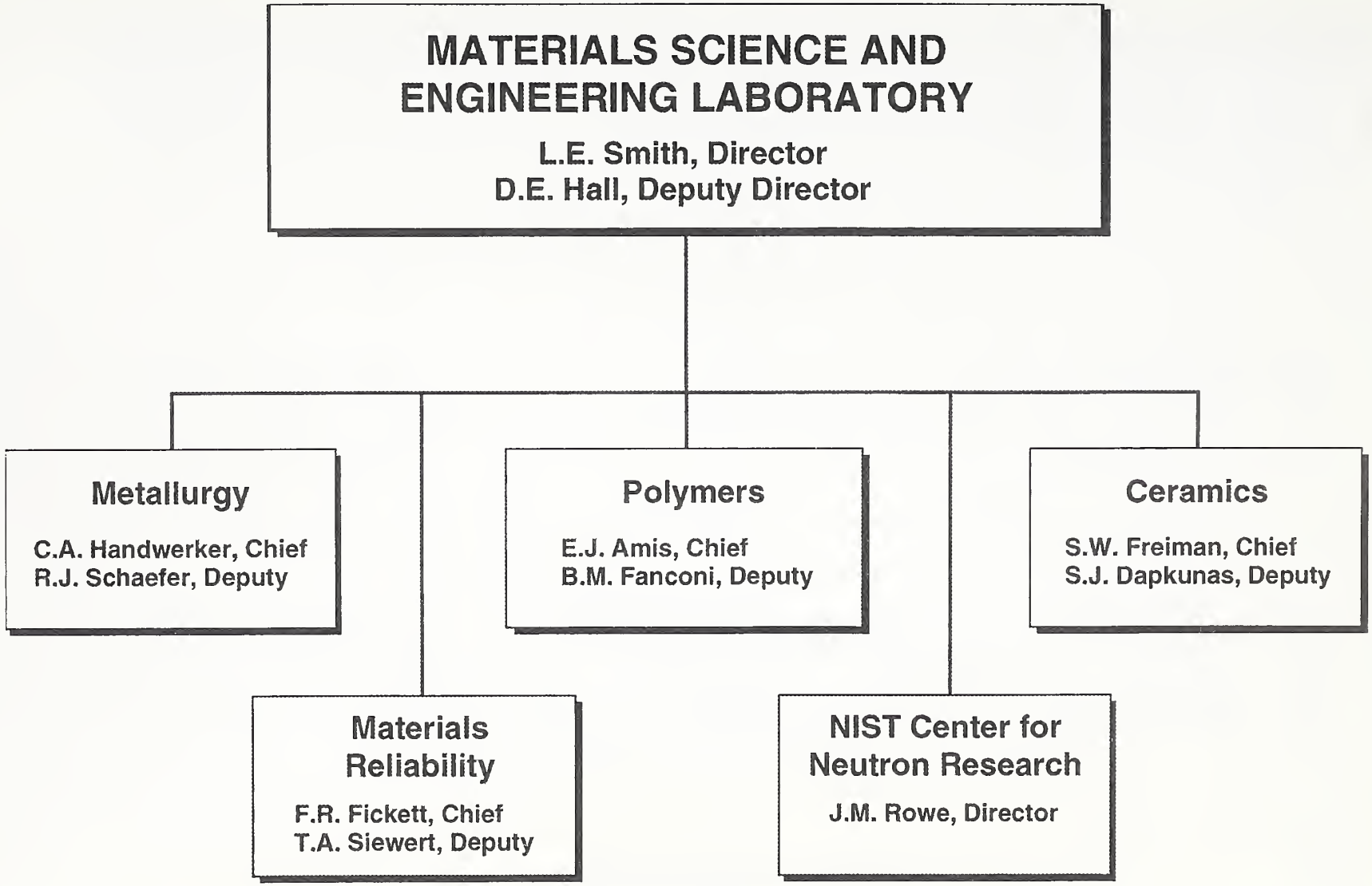
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Organizational Chart